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for February, 1937

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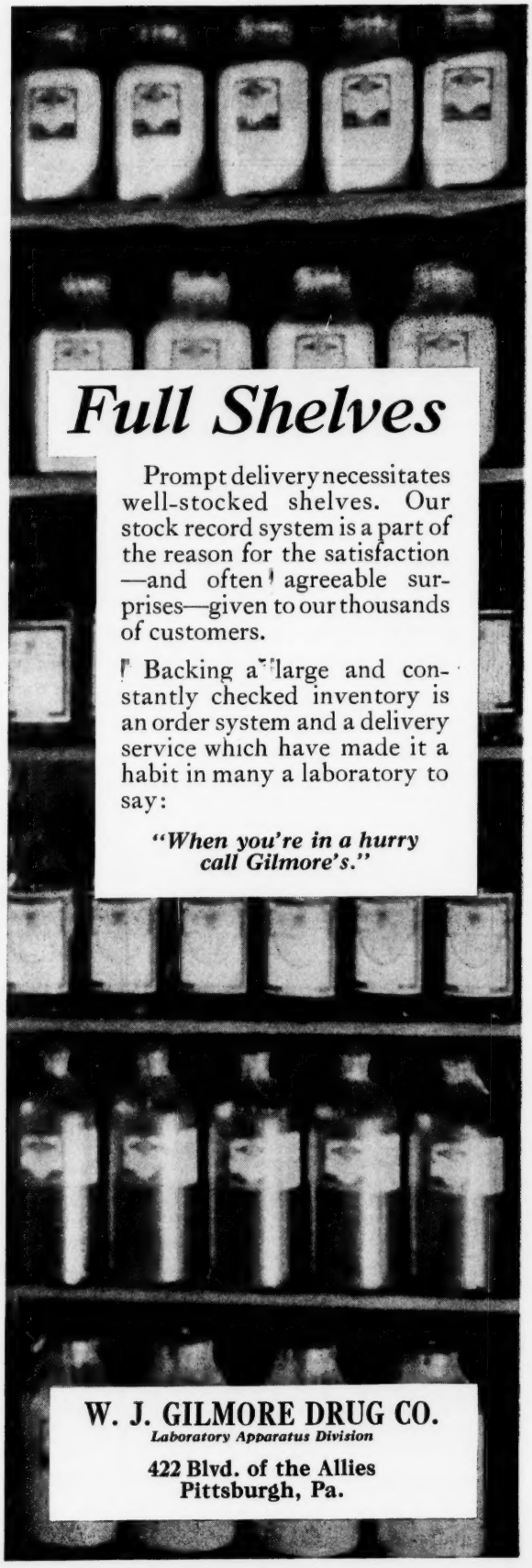

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CARL WILHELM SCHEELE (1742–1786)

"Swedish chemist and pharmacist. Independent discoverer of oxygen. He discovered arsenic acid, distinguished between nitric and nitrous acids, demonstrated the presence of tartaric, citric, malic, and gallic acids in plants, and discovered lactic and uric acids in the animal realm." (Mary Elvira Weeks, "The Discovery of the Elements," Mack Printing Co., Easton, Pa., 3rd ed., p. 45.)

This portrait, so far as known, the only existing likeness created during Scheele's lifetime, shows him at the age of about twenty-five years. The original, a painted ivory medallion, was discovered by S. Gullström on September 20, 1931, when he finally succeeded in running down a clue encountered in 1929. It is here reproduced by the kind permission of Arthur Nemayer, publisher of Otto Zekert's "Carl Wilhelm Scheele, sein Leben und seine Werke." For loan of a copy we are indebted to Dr. Ralph E. Oesper of the University of Cincinnati.

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EDITOR'S OUTLOOK

OPPORTUNITIES FOR THE "FOUR-YEAR" CHEMIST. Because we believe it to be of general interest we share with our readers the following correspondence. The first letter is from a professor of chemistry in a small midwestern college. The others are two of a number received from executives of national chemical and manufacturing corporations. They are representative of the general tenor of the replies to our inquiry in behalf of our first correspondent.

"The changes that have been inevitable as a result of the past few years of depression have, as far as one can observe, placed the new graduate in chemistry in a rather precarious situation. Today what is the young man fresh from college with his bachelor's degree in chemistry fitted to do? Are there direct openings in industry, business, or teaching for him? If so, what is the general nature of these positions and what is the best procedure for him to follow in making the necessary contacts? If these positions all require experience, how can the young man get the type of experience that is required as a prerequisite for the position?

"I am aware of the fact that the best students among the graduates should be encouraged to go on to do advanced work in chemistry in some recognized graduate school. This I do and am each year sending a few into advanced work. Most of these students have done well and now hold good positions. . . . But what of the student who is not financially able to continue his schooling, even though a good student? What is there available in chemistry for him to do? What is there available for the student who is a little too slow to keep pace with those in graduate school and yet does thorough, intelligent work in chemistry? He may be gifted in laboratory technique, but not quick enough to grasp the theory to be a successful graduate student. Does industry offer opportunities for him?

"The type of positions available to our graduates in chemistry before 1930 now, in many cases, seem to be closed to them because they do not have practical experience. This situation has caused me to try to devise some way by which our students will, to some degree, have this necessary experience. . . . I have been considering introducing a course in industrial analytical chemistry, conducting the course as an industrial laboratory. The object would be to teach the student rapid and accurate technique, rather than variety of methods, so that this will not have to be acquired after entering the industrial laboratory. Do you feel that such a course would be practical, and would it put the student in a better position to be located in an industrial laboratory upon graduation? Would such a course, properly conducted, be recognized as of value by the employment division of most industrial corporations?"

"I fully sympathize with [your correspondent's] situation. Many, if not most, of the collegiate institutions do not normally have the advantage of direct contact with the employing industries, due to the fact that these industries concentrate their recruiting efforts on the larger institutions and particularly those of university or engineering standing. A few employers are becoming wise to the fact that the best undergraduate training in the sciences is not necessarily found in the larger institutions from the standpoint of effective teaching of undergraduates. Some of the larger institutions definitely fall below the standard of a few of the smaller colleges.

"The best suggestion that I can make to [your correspondent] is that he attempt to make direct contact with the industrial relations or personnel executives of [several large chemical and manufacturing companies, names here omitted] and send them complete information concerning the personal qualifications and the training of two or three of his outstanding seniors.

"In my opinion, he should not attempt to sell the idea to the officers of any of these companies or any other employers that these men are chemists. That, I think, will defeat his purpose. Most, if not all, of these enterprises are at this time looking for young men with good personal characteristics whom they can put into their regular operating lines organizations for training. If these young men have good foundation training in their undergraduate courses, particularly in physics, mathematics and chemistry, he should have no difficulty in placing them this year, but they will not be placed ordinarily as chemists. They will be taken, if at all, on the basis of the individual's promise of development, and they are most likely to be placed upon direct productive operations. Some, of course, may be placed in laboratories as helpers. Each enterprise has its own system of training and development, in some instances consisting of a definitely scheduled program. . . .

"Concerning his suggested plan of introducing a course in industrial analytical laboratory work, I personally would recommend against it. If he is in a situation where he can give his undergraduates who have the desire to become chemists or chemical engineers a good grounding in fundamental physical sciences, including, of course, mathematics, that will be as much as can be done effectively in a four-year undergraduate course, and if he does this his men will be much better prepared if they go from his institution directly to industry to develop their individual capacities to the best advantage.

"I realize that there is a direct temptation on the part of the responsible teachers in collegiate institutions to attempt to introduce specialization in undergraduate years . . . but . . . after thirty years of experience in industrial work, during much of which time I have been responsible for employing young men from many institutions, I am today more firmly convinced than ever that any attempt at specialization in undergraduate work is unfair to the young man and undesirable from the standpoint of the employer generally."

"I think [your correspondent] exaggerates the difficulties with chemical graduates unable to carry through into graduate study. I know that such institutions as my own, and from conversation with competitive industry, there are always certain available openings in chemical plants for students who have been unable to take graduate work. As a matter of fact, outside of certain limited research opportunities, practically all of the college men hired each year are of this type. Attention is paid to the character of the fundamental education and not to the question of whether they have had practical experience or not, for this latter is not expected. These men are placed in the laboratories in the plants where they undergo training of a practical nature and superimposed upon what they are supposed to have learned in college. . . .

"After all is said and done the chemical industry employs a few thousand men in research and some hundred thousand in its factories. The opportunities for employment in the operating and management staffs are correspondingly many times greater than in the research laboratory and I am afraid that [your correspondent] has not properly appreciated the problem. Perhaps he is not instilling into his men the correct idea of the chemical industry and that is that it is after all a competitive manufacturing operation and untrained employes must start practically in competition with unskilled labor prepared to work routine and shift work and get their hands dirty. Their training, however, gives them a decided advantage in that they advance very rapidly if they have any of the latent characteristics that make for service. It may be that his system has brought about a most interesting situation in that I was just informed this week of two large chemical companies exhausting the graduates of an institution that never graduated anything but mechanical engineers. We all know the character of the material that this particular institution turns out, that it is sturdy, resourceful, well trained and not afraid of going to work on any job that promises a future. . . . When an institution makes a record for turning out competent men and instills in them an idea that there is still a lot to learn after they leave the school, and that they will have to buckle down to hard work, the chemical companies will grab those men frequently in preference to a chemical graduate who has been taught that his only service in life is to wear a white collar behind a clean laboratory table."

MRS. A. H. LINCOLN PHELPS *and* HER SERVICES *to* CHEMICAL EDUCATION*

MARY ELVIRA WEEKS AND F. B. DAINS

University of Kansas, Lawrence, Kansas

ABOUT a century ago, a gifted and broadly educated American woman, Almira Hart Lincoln Phelps, was devotedly teaching the natural and physical sciences and publishing textbooks on these subjects. Almira Hart was born at Berlin, Connecticut, on July 15, 1793. Her earliest teacher was her sister, Emma Hart Willard, author of "Rocked in the Cradle of the Deep." Almira taught in various rural schools and academies in Connecticut and New York, and in 1824, after the death of her first husband, Mr. Lincoln, she became a teacher of languages and sciences at the Female Seminary which Mrs. Willard had recently founded at Troy, New York.[1,2,3]

Although there were then few opportunities for women to engage in scientific study, there was at the Rensselaer Institute at Troy a very broad-minded professor of chemistry, the well-known Amos Eaton (1776–1842), who not only tolerated the presence of women in his classes but actually encouraged them. He gave lectures and laboratory instruction to several young women, including Mrs. Lincoln and Mrs. Willard.[4,5,6] Under his leadership Mrs. Lincoln became familiar with the chemical achievements of the greatest chemists of her day and learned to make successful lecture demonstrations before her pupils.[1]

In 1831 she married the Honorable John Phelps, who encouraged her to develop her literary talent. She published several textbooks on botany, geology, physics, and chemistry and various literary works. Her principal contributions to chemical literature were: a translation of a French dictionary of chemistry[7] (1830), "Familiar Lectures on Chemistry"[8] (1838), and "Chemistry for Beginners"[9] (1834).

From 1841 to 1856 Mrs. Phelps served as principal of the Patapsco Institute at Ellicott's Mills, Maryland, which trained young women to teach in the schools and homes of the South. In 1858 she entertained the annual convention of the American Association for the Advancement of Science at her home in Baltimore. The first woman to be elected to this organization was the astronomer Maria Mitchell; the second was Mrs. Phelps, and the third was her sister Mrs. Willard. Mrs. Phelps died on her ninety-first birthday, July 15, 1884. Dr. Emma L. Bolzau's dissertation[10] on her life and work is a fine tribute to her memory.

FIGURE 1.—ALMIRA HART LINCOLN PHELPS, 1793–1884

The dictionary which Mrs. Lincoln Phelps translated was not written by Vauquelin, as has sometimes been stated, but by MM. Brismontier, Le Coq, and Bois-

* Presented before the Division of History of Chemistry at the Kansas City meeting of the A. C. S., April 14, 1936.

[1] "Mrs. A. H. L. Phelps," *Barnard's Am. J. Educ.*, **17**, 611–22 (Sept., 1868).

[2] DUMAS MALONE, "Dictionary of American Biography," Charles Scribner's Sons, New York, **1934**, vol. 14, pp. 524–5. Article on Mrs. Phelps.

[3] MRS. A. W. FAIRBANKS, "Emma Willard and her pupils or fifty years of Troy Female Seminary, 1822–1872," Mrs. Russell Sage, New York, **1898**, 895 pp.

[4] LOUISE SCHUTZ BOAS, "Woman's Education Begins," Wheaton College Press, Norton, Massachusetts, **1935**, pp. 185–94.

[5] P. C. RICKETTS, "Rensselaer Polytechnic Institute," Rensselaer Inst. Engrg. and Science Series, No. 45, 1–32 (Nov., 1933).

[6] R. P. BAKER, "A chapter in American education. Rensselaer Polytechnic Institute, 1824–1924," Charles Scribner's Sons, New York, **1925**, pp. 10–26 and 48–68.

[7] MRS. ALMIRA H. LINCOLN, "Dictionary of chemistry containing the principles and modern theories of the science, with its application to the arts, manufactures, and medicine, for the use of seminaries of learning and private students," G. and C. and H. Carvill, New York, **1830**, 531 pp. (Translated from "Le dictionnaire de chimie approuvé par Vauquelin," with additions and notes by Mrs. Lincoln.)

[8] MRS. ALMIRA H. LINCOLN PHELPS, "Familiar lectures on chemistry for schools, families, and private students," F. J. Huntington and Co., New York, **1838**, 448 pp.

[9] MRS. A. H. LINCOLN PHELPS, "Chemistry for beginners," F. J. Huntington and Co., New York, **1839**, 216 pp.; *ibid.*, Huntington and Savage, New York, **1849**, 216 pp.

[10] EMMA L. BOLZAU, "Almira Hart Lincoln Phelps. Her life and work," University of Pennsylvania, Philadelphia, **1936**, 534 pp.

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duval. It received, however, the sanction and approval of the illustrious Vauquelin, and the translation was enthusiastically supported by Amos Eaton and Benjamin Silliman, Senior. Since the French edition had been published in 1826, Mrs. Lincoln Phelps modernized the work with additions from the works of Andrew Ure (1778–1857), professor of chemistry at Glasgow, John White Webster (1793–1850), professor of chemistry at Harvard University, Jacob Green (1790–1841), Philadelphia chemist and naturalist, Silliman the Elder, and "the latest French writers."

The book opens with a brief outline of the history of chemistry. Among the modern chemists are mentioned Sir Humphry Davy, John Murray, W. T. Brande, Thomas Thomson, J. J. Berzelius, L. N. Vauquelin, C. L. Berthollet, J. L. Gay-Lussac, L. J. Thenard, J. B. A. Dumas, P. L. Dulong, Joseph Pelletier, and the Americans: Benjamin Franklin, Robert Hare, Silliman the Elder, and Amos Eaton.

The nineteenth-century attitude toward scientific careers for women is expressed as follows: "From the nature of chemical experiments. . . . woman may not aspire to add to the stock of chemical science discoveries of her own; but. . . she may dare to raise the curtain which conceals the operations of nature and, entering her laboratory, behold the grand experiments which are there exhibited. . ."[7]

"Chemistry," she hopefully continues, ". . . is now open to the researches of all. Nature. . . has no longer her secrets; Chemistry has discovered the phenomena which operate in her atoms, calculated their effects, traced their bounds, and insulated [isolated] their elements. Such are the rapid and wonderful results of chemical experiments that one half hour's attention may suffice to throw light upon some of the most obscure mysteries of nature."[7]

From the article on *Oxygen* one learns to appreciate some of the difficulties that had to be overcome before this gas could be successfully used in medicine. "Pure oxygen is employed only in Chemistry, though at the period of its discovery physicians entertained great hopes respecting its utility in the cure of diseases, particularly that of the lungs; but experience proved that it produced upon these organs too great a degree of excitement and at length caused the destruction of the animals who for any length of time respired it."[7]

The very brief article on *Synthesis* contains the statement: "We are able by synthesis to imitate most of the compounds in the inorganized kingdoms; but nature, or rather the Author of nature, can alone perfect the compounds of the organic kingdom."[7] Although Mrs. Lincoln Phelps was well versed in the American, British, and French literature of chemistry, her knowledge of German achievements appears to have been less thorough. She was apparently unaware in 1830 that Wöhler had synthesized urea in 1828; in fact, even in the 1849 edition of her "Chemistry for Beginners" the same view is again expressed: "The *living principle* both in plants and animals is concealed from the search of man, although he has been prying into the mystery ever since Satan tempted our first parents to disobey God. . . All that can be done in organic chemistry is to examine, by means of chemical analysis, the elements of which bodies are composed and to learn the various combinations which exist in animal and vegetable substances."[9]

Mrs. Willard had for some time collected notes on culinary chemistry suitable for an elementary textbook. Since she could not find time to write the book herself, she intrusted these notes to Acting Professor William F. Hopkins[11] (1802–1859) of the United States Military Academy, who began the work, but relinquished it, placing his incomplete manuscript at the disposal of Mrs. Lincoln Phelps. In 1838 she published the completed work under the title "Familiar Lectures on Chemistry" and dedicated it to Robert Hare. It contains illustrations and careful descriptions of various instruments which he devised. In the preface she gives as her object the desire to make physical science "more generally appreciated, especially by her own sex."

The book consists of thirty-two lectures based on "the standard authors of the science," especially "Hare, Silliman, Turner,* Berzelius, and Thenard." In the third lecture, on "vaporization, ebullition, etc.," Mrs. Phelps mentions Faraday's recent success in liquefying "carbonic acid." "A French Chemist [M. Thilorier] . . ," she adds, "announces that he has also obtained it in a *solid state* . . . The first instance of a *gas* becoming *solid* and concrete is so much the more remarkable as it relates to a gas to liquefy which requires the most powerful mechanical action, and which resumes with great rapidity its gaseous state when the compression is removed."[8]

In lecture six, on electricity, Mrs. Phelps mentions Benjamin Franklin's one-fluid theory, which held sway in the United States and Great Britain, and C. F. Du Fay's two-fluid theory, which prevailed on the European continent. In a lecture on galvanism, she explains the three prevailing theories of voltaic action: the electrical theory of Volta, the chemical theory supported by Dr. Wollaston, and the electrochemical theory of Davy, giving her preference to the last of these.

In her lecture on the halogens, she agrees with Silliman that "it seems premature to place fluorine, a principle purely hypothetical, along side with chlorine and iodine, whose distinct existence and peculiar energy are manifested in so many remarkable forms . . . This body has never been seen in an insolated [sic.]state."[8] In her "Chemistry for Beginners," she says, "You will perhaps smile when you learn that chemists have placed among the elements a substance which does not exist or, at least, which has never yet been obtained.

---

[11] "Appleton's cyclopaedia of American biography," D. Appleton and Co., New York, **1892**, vol. 3, pp. 259–60; J. H. BROWN, "The cyclopaedia of American biographies," James H. Lamb Co., Boston, **1901**, vol. 4, p. 153.

* Probably Edward Turner (1798–1837), chemist at Edinburgh and London.

But such is the case, and the name which they have given to this imaginary element is *fluorine* . . . We shall not attempt to say anything about this fluorine, which, like the hero of a novel, has but an imaginary existence."[9]

Chemists of her day were not agreed as to whether air was a mixture or a compound. Some argued that, if it were a mixture, the heavier of its two principal constituents would settle to the bottom. Mrs. Phelps explains, however, that "the investigations of Mr. Dalton and especially of Dr. I. K. Mitchell [probably Dr. John Kearsley Mitchell (1793–1858)] of Philadelphia have proved that gases have a strong tendency to diffuse themselves through each other, contrary to gravity, . . . and this, too, when no chemical affinity can be supposed to exist between them." After giving other good reasons for her belief, she concludes, "It seems, therefore, highly probable that the atmosphere is a mere mixture of its components."[8]

Nineteenth-century methods of food preservation make one appreciate modern refrigeration. "Charcoal," says Mrs. Phelps, "has remarkable antiseptic power, preventing the putrefaction of meat and vegetables . . . Tainted meat becomes sweet after being sometime covered with it; and by filtration through its powder, putrid water is rendered pure."[8] Another example of the sanitary methods of her day may be cited from the "Chemistry for Beginners." "[Muriatic acid] . . . is very useful in a sick room, by destroying the disagreeable odours and preventing contagion . . . . All contagion is conveyed by means of bad air, or unwholesome gases."[9]

Students who learned their organic chemistry from the "Familiar Lectures" had no need to burn the midnight oil. "Carbon and hydrogen," says Mrs. Phelps, "form at least six definite compounds, and from the experiments of Mr. Faraday, it is probable that some more compounds of them exist, which have not yet been obtained separately."[8]

Mrs. Phelps often chooses her examples of chemical phenomena from places near at hand. "There is a rivulet," says she, "running through the village of Fredonia, and another which passes by Portland Harbor, both in Chautaugue [sic.] County in the state of New York, from the waters of which bubbles of light carburetted hydrogen gas [methane] are constantly rising. The supply of gas at Fredonia is sufficient for lighting the houses of the village . . . The light house on Lake Erie at Portland harbor is completely supplied with gas obtained from the rivulet above mentioned."[8]

She also relates another interesting incident connected with the history of gas lighting. "Some years ago," says she, "an attempt was made by Mr. Gordon to render oil gas lamps portable, for domestic use. His plan was to compress into strong copper vessels . . . about thirty times their volume of gas: by means of a jet and stop cock, the gas might be allowed egress, and might be burnt as it issued. The project was at first quite successful, and his lamps were even used on stage coaches; but it was found, that by this pressure, a portion of the gas was condensed into a fluid resembling an oil . . . The increase of expense caused by this circumstance caused this mode of using oil gas to be abandoned. The *oil like* liquid was found by Mr. Faraday to consist of several definite compounds of carbon and hydrogen in a state of mixtures."[8] This is an allusion to Faraday's discovery of benzene ("bicarburet of hydrogen").[12]

In the "Chemistry for Beginners," Mrs. Phelps states, "Combinations of carbon with simple bodies are called carburets; the most important of these is *carburetted hydrogen* . . . Those of you who have walked

FAMILIAR LECTURES

ON

CHEMISTRY.

FOR SCHOOLS, FAMILIES, AND PRIVATE STUDENTS

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AUTHOR OF "FAMILIAR LECTURES ON BOTANY," "FAMILIAR LECTURES ON NATURAL PHILOSOPHY," "FEMALE STUDENT," &c. &c.

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1838.

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FIGURE 2.—TITLE-PAGE OF MRS. PHELPS'S "FAMILIAR LECTURES ON CHEMISTRY"

out of an evening in the principal streets of New York . . . must have noticed the beautiful and brilliant lights

[12] FARADAY, M., "Experimental researches in chemistry and physics," Taylor and Francis, London, **1859**, pp. 154–74; THOMAS MARTIN, "Faraday's diary," G. Bell and Sons, London, **1932**, vol. 1, pp. 197–234; FARADAY, M., "On new compounds of carbon and hydrogen, and on certain other products obtained during the decomposition of oil by heat," *Annals of Phil.*, **27**, 44–50 (Jan., 1826); *ibid.*, **27**, 95–104 (Feb., 1826). Read June 16, 1825.

which illuminate the streets . . . *These lights burn without any wicks; they are caused by the combustion of gas.*"[9]

Her textbooks abound in mildly humorous illustrations of chemical phenomena. In discussing the physical properties of iron, she says, "So exceedingly ductile is it that it may be drawn into wires finer than human hair; and according to Fourcroy periwigs have been made in France of such wires . . . Mrs. Fulhame gilded ribbons by moistening them with a

TO

Dr. ROBERT HARE,

To whose inventive genius, Chemistry is indebted, for many of its most valuable illustrations, and whose profound researches have added stability, and elevation to the Science, this volume is, by permission, and with deference, most respectfully dedicated

by

THE AUTHOR.

Brattleborough, Vt., Oct. 1838.

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FIGURE 3.—DEDICATION OF MRS. PHELPS'S "FAMILIAR LECTURES ON CHEMISTRY"

solution of muriate of gold by means of a camel's hair pencil, and holding them over hydrogen gas as it was evolved."[8]

Mrs. Phelps advises her students against the use of pedantic expressions: "Chemists," says she, "seeing the advantage to science of a regular momenclature, have undoubtedly gone too far in attempting to introduce technical names into common language; and our respect for science would scarcely be sufficient to repress a smile, should a person wishing for water and sugar, call for the protoxide of hydrogen combined with hydro-carbonous oxide."[8]

Two editions of the "Chemistry for Beginners" were examined, one of 1839 and one of 1849. The latter is apparently merely a reprint, with few, if any, alterations. Mrs. Phelps states that she has attempted "to present the elements of the science in a popular and attractive form, without offending the scholar"; which, by the way, is no easy task. Some of the engravings are "from original designs . . . and some are copied from the works of Hare and Silliman, with the consent of these gentlemen."[9] She also thanks Robert Hare "for his polite and encouraging attentions in forwarding to her some recent publications of his own, containing drawings of newly invented and highly useful apparatus."[9]

At the Troy Female Seminary, Mrs. Phelps required her pupils to prepare experiments and give lectures on assigned subjects before the class. Although this did not lighten her teaching load, it had, says she, "a beneficial effect on the mind of the pupil."

Even in this book intended for very young pupils, Mrs. Phelps presents chemistry as a living, growing subject and often compares opposing theories. After introducing the term *muriate of soda*, for example, she adds in a footnote: "We are met by a difficulty on the threshold of the science; since common salt is of late considered as a *chloride of sodium*. But we are attempting to divest science of technicalities as much as possible; we must therefore use such terms as are most generally received, without attempting to reconcile opposing theories."[9]

In discussing the applications of chemistry she says, "This science bears an important relation to housekeeping . . . in the making of gravies, soups, jellies and preserves, bread, butter, and cheese, in the washing of clothes, making soap, and the economy of heat in cooking, and in warming rooms . . .To females, then, some knowledge of Chemistry must be very desirable."[9] In another place she states: "Every economical family save all the bits of fat which are unfit for cooking, in order to use for making soap. The ashes which are collected daily from the fireplaces and stoves are saved for the same purpose." A footnote explains that "In cities it is generally thought economical to dispose of the ashes and grease to the soap manufacturer and receive soap in return. In the country it is necessary for every family to make their own soap."[9]

Mrs. Phelps also mentions another household industry of her day: "Among farmers in the country," says she, "it is very common for each family to manufacture their own starch. The green ears of Indian corn or potatoes are grated into large tubs of water; the starch settles at the bottom; the water is then poured off . . . The process is repeated until the starch is perfectly clean and white; it is then laid on large platters and

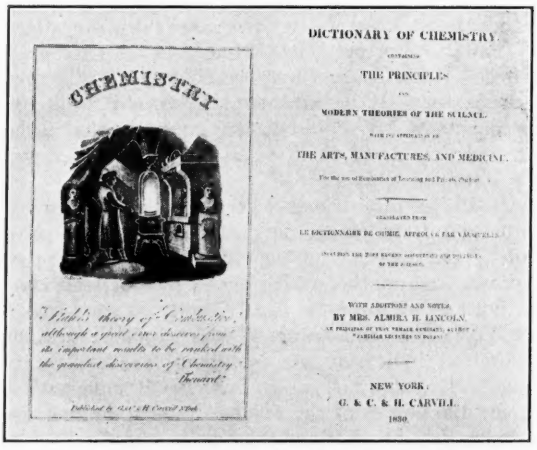

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FIGURE 4.—FRONTISPIECE AND TITLE-PAGE OF THE DICTIONARY OF CHEMISTRY WHICH MRS. LINCOLN (PHELPS) TRANSLATED FROM THE FRENCH

The names on the busts are Fourcroy and Lavasoir (sic.).

dried in the sun. There are now many starch manufactories; near Utica is a village where the business is extensively carried on. Under the name of Poland starch, much that is made in the United States is sold."[9] Yeast was also produced in the home by

allowing vegetable substances to ferment, and "Every housekeeper who does not live where she may procure yeast at the distillery or brewery should be careful to keep by her a quantity of this article."[9]

Mrs. Phelps gives a striking conception of the awe with which electricity was then regarded: "The *metals* are conductors—for this reason it is unsafe during a thunder storm which is very near for people to wear spectacles with gold or silver bows, watches, thimbles, buckles in shoes, or indeed any metallic substance . . . Feathers and hair are *non-conductors*—for this reason a feather bed or mattress is a safe position in a thunder storm . . . But after all our care, we must ever reflect that life is in the hands of Him who gave it . . . Our own countryman, Dr. Franklin, was the first who proved that lightning and electricity were the same."[9]

After giving a fine description of Davy's safety lamp, Mrs. Phelps comments: "As the miner now goes forth to his daily toil with his safety lamp, . . .how ought he to bless the benefactor to whom he is indebted for this security! But it is probable that very few of this class of persons ever heard his name, for they are obliged to labour very hard, and have no means of gaining knowledge like the young persons who are now studying this book."[9]

The subject of hydrogen sulfide enables her to give some sage advice regarding cosmetics. She explains that compounds of lead and bismuth are "used as the basis of the paints or cosmetics which are used by silly females under the mistaken idea of improving their complexions," and adds: "Now it would be a very unpleasant circumstance to a beautiful painted lady, walking near a sulphur spring, . . . to have her colour suddenly changed . . . ; but this is a risk that must always be incurred by those who use cosmetics prepared from mineral substances."[9]

Mrs. Phelps closes the book with the optimistic words: "You have now learned to understand chemical language. The Beginner in Chemistry . . . is now prepared to understand chemical books and lectures and to make his own researches into the great volume of nature!"[9,†]

† It is a pleasure to acknowledge our indebtedness to Miss Eva V. Armstrong, curator of the Edgar Fahs Smith Collection at the University of Pennsylvania, who loaned us copies of Mrs. Phelps's textbooks and sent us Dr. Emma L. Bolzau's dissertation.

MODERN METHODS *of* METAL FINISHING[1]

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IN THIS age of metals it is not surprising that the chemical engineer is developing numerous methods of finishing which greatly increase the usefulness of the metals. At the present time the finishing of metals is carried on chiefly to increase their resistance to corrosion or abrasion and to improve their appearance.

Finishing to Improve Corrosion-Resistance and Appearance.—Much has been written about the corrosion of metals, and rightly so. Iron, which is by far the most important metal at the present time, is particularly subject to corrosive attacks, not only by many strong chemicals, but also by comparatively mild materials, such as those which are present in the ordinary atmosphere. Thus, when exposed to the atmosphere, iron soon becomes unattractive and its usefulness is frequently decreased to a great extent.

The most obvious way to avoid this difficulty is to cover the iron with a film of some material which is less susceptible to the action of corrosive substances. This film may be of

(1) another metal such as copper, tin, zinc, nickel, or chromium,

(2) a compound of iron such as the oxide or phosphate,

(3) non-ferrous inorganic material such as vitreous enamel,

(4) a substance which is entirely organic or else a combination of organic and inorganic materials such as paint, varnish, lacquer, or rubber.

Another method of decreasing the corrosion of iron is to add other metals, such as nickel, chromium, and silicon to it to form an alloy. Strangely enough, a number of these alloys are less noble than iron itself and yet, under many conditions, they corrode less. One important reason for the corrosion resistance of such alloys is the fact that extremely thin "natural finishes," probably oxidic in nature, are formed upon their surface.

Then, in many cases, the properties of iron and its alloys make it necessary to abandon them entirely and to choose some other metal or alloy which does possess the desired properties. The use of such metals as nickel, aluminum, and magnesium, and of such alloys as brass and monel metal is increasing annually.

[1] A course of lectures in Metal Finishing is given by the author in the Department of Chemical Engineering at Columbia University.

Some of these metals (as copper, nickel, and aluminum) are protected by "natural finishes" more or less similar in nature to those on the surface of the iron alloys already mentioned. Some of them (as aluminum, zinc, magnesium, and their alloys) are frequently coated with another metal or with some material of the paint or lacquer type.

An oxide film exhibiting many important properties may be produced electrolytically on the surface of aluminum and some of its alloys. This film is very hard, is resistant to certain types of corrosion, will withstand rather high voltages and is capable of being colored.

Finishing to Improve Resistance to Abrasion.—The resistance of iron to abrasion may be increased by processes similar to those used to increase its resistance to corrosion and to improve its appearance. It is well known that electroplating iron with chromium will greatly increase the resistance of the iron to abrasion. Also, if a film consisting largely of iron compounds such as the carbide or nitride is formed on the surface of iron, the hardness will be increased.

The addition to iron of certain metals such as tungsten will improve its resistance to abrasion. High-speed steel containing as much as eighteen per cent. of tungsten will retain its hardness even at quite high temperatures.

Sometimes it is advisable to use some non-ferrous material. For example, certain alloys composed of cobalt, chromium, and tungsten (called stellite) are becoming increasingly well known for their hardness, even at red heat.

Coating with Another Metal.—One metal may be coated with another metal in a variety of ways. If the coating metal has a comparatively low melting point, it may be applied in a molten condition by the process of hot dipping. The nobler metals are frequently plated by electrodeposition from aqueous solutions of their compounds. Hot metal powder may be applied by cementation processes. Finally, almost any metal may be sprayed not only upon metal surfaces but also upon materials as easily destroyed as paper.

Coatings of Iron Compounds.—The pleasing appearance of the surface colors produced by heating iron in the air is well known. Other iron oxide coatings which are valuable because of their protective properties and their appearance may be produced by processes which are somewhat more complicated.

The importance of phosphate coatings on iron, either alone or beneath a film of paint, enamel, or lacquer, is rapidly increasing.

Iron carbide, iron nitride, or a combination of the two can be produced on the surface of iron, depending upon the process used.

Vitreous Enamels.—Although vitreous enamels were used as long ago as three or four centuries before Christ, the production of enameled metals is one of the most complex procedures in the field of metal finishing, and much remains to be learned about it. Perhaps the most important requirement in order to obtain good results in this field is a knowledge of high-temperature chemistry.

Paints, Varnishes, Lacquers, Rubber.—At the present time the amount of research which is being carried on in this field is enormous. There is the greatest rivalry between enamels and lacquers and between other kinds of finishes in this same general field. Also, there is a keen competition between these finishes and the metallic coatings.

The production of new alloys, many of which must be protected by some kind of finish, has still further added to the feverish activity of the paint, varnish, and lacquer chemists.

Rubber-coated metal is being used extensively, especially in the production of containers for highly corrosive materials.

Importance of Clean Metal Surfaces.—One important requirement is common to most of the different metal finishing processes. The surface of the iron or other basis metal must be clean. It must not only be free from metallic oxides but also from traces of grease if the best results are to be obtained. The oxides may be removed by chemical or electrochemical pickling and the grease and other dirt, which is frequently associated with it, by chemical or electrochemical cleaning. There are many possible cleaning and pickling procedures, and it is necessary to choose the one which best fits the properties of the basis metal which is to be finished.

Cladding.—It has been mentioned already that either non-ferrous metals or alloys of iron may be used advantageously for many purposes. Unfortunately, these materials are frequently very expensive, and for that reason their use is much more limited than it otherwise would be.

For a number of years attempts have been made to "clad" ordinary, inexpensive iron with a fairly thin coating of a more expensive metal. In this way the desired properties of the expensive material could be obtained at a more reasonable price. Until recently it was difficult, if not impossible, to obtain a sufficiently strong weld between many of the cladding metals and the backing of ordinary iron due to the impossibility of eliminating the "natural finishes" from the surface of the cladding metals. Now, however, a method has been developed which does eliminate these "natural finishes," with the result that excellent welds may be produced quite readily. It is now possible to obtain ordinary iron clad with such metals and alloys as nickel, stainless irons, 18–8 chromium-nickel steel, high carbon steel, high speed steel, and stellite. Also, some of the cheaper metals and alloys such as copper and brass may now be clad with noble metals such as gold, silver, and platinum.

It is hoped that enough has been written in this brief outline to show the extent and importance of the rapidly expanding field of metal finishing.

HISTORICAL DEVELOPMENT *of the* CONCEPTION *of* CHEMICAL ELEMENTS

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L'habitude d'une opinion produit souvent une conviction complète de sa justesse; elle en cache les parties faibles et rend l'homme incapable, d'apprécier les preuves contraires.—J. J. Berrelius. "Théorie des proportions chimiques," Deuxième édition, 1835, page 35.

✦ ✦ ✦ ✦ ✦ ✦

ELEMENTS are ultimate component parts which constitute a given object. To obtain a knowledge of them the original object must be decomposed by analysis: the ultimate undecomposable products of analysis are the immediate component parts, objective elements, which in turn serve for the deduction of abstract elements. Analytical methods are being continually perfected in every science. Thus it may happen that at a certain moment of time the existing elements are decomposed into new ones, and these may give rise to new abstract elements.

The object of chemistry is the investigation of natural and artificial bodies and of substances composing them. Their ultimate component parts are chemical elements (1) which must be chemically undecomposable into simpler substances and (2) which must be immediate component parts of a given substance. Now the investigation of substances produced by nature and art, from matter, occupied the attention of philosophers from the very earliest times. Thus the history of the development of the conception "chemical element" covers more than two millennia, and in this short summary I can touch only upon some of the principal facts.

I. It seems that a very old conception of the constitution of matter is contained in the atomic theory. This postulated that indivisible atoms of matter moving in a vacuum were the elements of all bodies of nature.

Another conception was brought forward, perhaps somewhat later, being developed chiefly by Aristotle (IV century B.C.), who denied the existence of a vacuum and taught that all bodies are composed of qualities: hot-cold, wet-dry, perceptible to our senses and embodied in the four elements, fire (dry and hot), air (wet and hot), water (wet and cold), earth (cold and dry). These Aristotelian elements were almost universally accepted up to the second half of the XVIII century A.D. But chemists early adopted other elemental qualities. These were sulfur (quality of combustibility) and mercury (quality of volatility), mentioned already by the early Greek chemists, more fully described by Djabir ibn Hayan (end of VIII century A.D.), and salt (quality of incombustibility, as evidenced by a residue left after calcination), introduced by Paracelsus (beginning of XVI century). In the early years of the XVIII century sulfur coëxisted with phlogiston: this element-quality is characteristic of the XVIII century, being used for the explanation of all chemical phenomena known at the time. The theory of phlogiston allowed one (for the first time in the history of chemistry) to systematize chemical knowledge from one point of view.

Under the influence of new ideas brought forward by R. Boyle and described in section II, and of the gradual extension of quantitative methods of work, philosophers began to regard the elemental qualities as substances. Jung in 1730 was the first to hold phlogiston to be a weightless substance conferring to its compounds a loss of weight. Others began to regard the Aristotelian qualities, fire, water, air, earth, as substances of the same name, and this point of view became universal during the last decades of the XVIII century. It was these elemental substances that were overthrown by Lavoisier who showed that air, water, earths were compounded bodies, that the substance phlogiston was a product of imagination. He introduced instead the elements of Boyle, the simple or uncompounded bodies. But this chemical revolution was not brought to a logical conclusion by Lavoisier, inasmuch as he left among the new elements two substances without weight—light and heat (caloric). This was doubtless due to the influence of physics, where immaterial fluids were used to explain such phenomena as light, heat, electricity, etc. In the first decades of the XIX century we find in textbooks of chemistry these more modern elemental qualities. Light was discarded in the early forties from chemistries, caloric in the fifties, and the electrical fluids in the early sixties. But physicists retained the electrical fluids up to the end of the XIX century. Thus some of the elemental qualities persisted, in a modern dress, almost up to our times.

II. In 1661 R. Boyle gave a new definition of a chemical element in the following words (Sceptical Chymist): "I now mean by elements ... certain primitive and simple, or perfectly unmingled bodies, which not being made of any other bodies, or of one another,

are the ingredients of which all those called perfectly mixt bodies are immediately compounded, and into which they are ultimately resolved." He indicated also chemical analysis as the means of deciding if a body was simple or "mixt." During the XVIII century, as stated above, the elements of Boyle began to find recognition by chemists, and were definitely introduced by Lavoisier in the years 1787–89.

Lavoisier gives several definitions of a chemical element:

(*a*) An element is every simple substance undecomposed by chemical analysis and giving in chemical reactions products always having a greater weight than itself. This is the element of R. Boyle.

(*b*) An element is the "base" of a gas or of another body. These "bases" (or "principles," another name employed by Lavoisier) are undecomposable substances which cannot be directly observed, as we know them only in compounds with caloric or with other bases. Thus the base oxygen is contained in the gas oxygen combined with caloric, and in different oxides combined with other "bases." The "base" carbon forms different simple bodies (diamond, charcoal) and compounds, such as carbonic acid gas.

(*c*) "If we understand by elements simple and indivisible molecules of bodies, it is probable that we do not know them."

III. The same three points of view on the nature of elements were current during the XIX century. We will consider them under the same headings.

(*a*) Very many scientists, even up to the present day, hold the elements to be simple substances. It is enough to examine such recently published fundamental works as the latest edition of F. Ephraim's "Inorganic Chemistry," or the "Physico-chemical Tables" of Landolt-Börnstein (issued in October, 1935), to see that under the heading "properties of chemical elements" the properties of simple substances are described. These authors evidently do not take into account the existence of allotropic modifications, discovered by Lavoisier for carbon and described in the XIX and the XX centuries in great numbers. Such modifications having identical chemical properties and different physical ones show that they are composed by the same element, but that they themselves are *not* chemical elements. Indeed the simple bodies, or simple substances, as they are being called nowadays, have only one of the two characteristics of a chemical element: they are chemically undecomposable, but they are not contained as such in compound substances. This was the opinion of Lavoisier, stated by some before him. It is accepted today by practically all chemists.

(*b*) During the last century the chemical elements begin to be identified with the "bases" or "principles" of Lavoisier. Thus already A. Fourcroy in his "Système des connaissances chimiques" (1801) points out that a principle cannot be separated as such, but it can be measured, weighed, combined; it is partly an abstract entity. I will retain the old word "principle" in order to distinguish the two different conceptions—that of principle and that of simple substance (F. Paneth in 1931 proposed for principle the name "primary substance," Grundstoff).

There is no question as to principles being true chemical elements, since they are chemically undecomposable immediate component parts of simple and compound bodies, thus completely satisfying the definition of a chemical element. They possess chemical properties, but few physical ones, the chief (from the chemist's point of view) being their weight. Almost every chemist, even today, confuses the principles and the simple substances, designating both these different things by the same term "chemical element." The question as to the nature of chemical element was discussed at the first International Chemical Congress in 1860. No resolutions were passed, but the majority of the members seemed to consider the principle as chemical element. Since that date the leading chemists, as, for instance, D. I. Mendeléeff, draw the distinction between simple substances and principles and hold only these last to be chemical elements. Thus the periodic system of Mendeléeff is a system of principles, not of simple substances.

(*c*) Lavoisier's remark about elements being simple and indivisible molecules of bodies is the keynote to the amazing developments which this point of view received in the XIX century. These developments were primarily the result of several important quantitative facts established by Lavoisier and his successors: (1) two principles can sometimes form *several* distinct compounds with each other; (2) in such compounds, if the weight of one principle is taken as constant, the weights of the second principle are proportionate to simple numbers (W. Higgins, 1789; J. Dalton, 1803, and seq.); (3) the composition of a chemically pure substance is constant (J. Proust, C. Berthollet, 1803). These facts were explained by W. Higgins in 1789, by J. Dalton in 1808, by the assumption that *atoms of simple bodies combine with each other.* All atoms of a given simple body were held to be identical as regards dimensions and weights, this last remaining without change during chemical interactions. Atoms of different simple bodies were thought to differ by weight and dimensions.

Thus W. Higgins and J. Dalton brought together the conception of chemical element-simple substance of Boyle [(*a*) of Lavoisier] with that of abstract atoms. They postulated the existence of as many kinds of atoms, differing by weight and chemical properties, as there were simple bodies.

Further developments of this doctrine were due to the introduction of the conception of *chemical molecule* as the smallest quantity of a substance having all the chemical properties of this substance, and composed of atoms. Proposed by A. Avogadro (1811) and A. Ampère (1814) in order to explain the work of J. Gay-Lussac, who studied the chemical properties of gases, it was developed by M. Gaudin (1831), Ch. Gerhardt, and Aug. Laurent (soon after 1840). The molecular theory was definitely adopted on the recommendation

of S. Cannizzaro in the historical first International Chemical Congress of 1860. Henceforth, all substances are considered by chemists to consist of molecules, not of atoms as such; an atom is the smallest quantity of an element (principle) in the molecules of its compounds. This Congress marks the date when *atoms were brought into relation with principles*, not with simple substances, as heretofore. Chemistry from 1860 onward is a science of molecules and of atoms, accepted by chemists "as if they existed." The amazing progress of organic chemistry, dating from the early sixties of last century, is due not only to the synthetic methods discovered by M. Berthelot, but in a great measure to the introduction of molecules.

IV. The very beginning of the XX century brought forward proofs of the real existence of molecules and of atoms, and such proofs have repeatedly been advanced since that epoch. X-ray analysis (1912–1914) has shown that crystals are formed by atoms and ions: consequently principles, as component parts of all bodies, are contained in them in the form of atoms and ions. Atoms and ions are best characterized by their atomic numbers, first introduced by Rydberg in 1897. The atomic numbers, as shown by H. Moseley (1913), are easily calculated from the wave-lengths of the lines of X-ray spectra of the principles. It was he who established the total number of elements (principles) up to uranium inclusive (92), and who pointed out the number of rare earths' elements.

The physical significance of the atomic number was demonstrated by E. Rutherford and J. Chadwick (1919–1920): this constant is the value of the positive electric charge of the atomic nucleus, as was supposed by H. Moseley, and indicates the number of the planetary electrons of the atom. The atomic number is the same for all atoms and ions of a given principle.

The study of mass spectra of elements, begun by F. Aston in 1920, giving the mass of each individual atom, has brought to light an utterly unexpected fact: there are many principles, each of which has atoms of different mass. Every separate kind of atoms having identical masses and atomic numbers constitutes one isotope (F. Soddy, 1913). Several isotopes having the same atomic number and identical chemical properties form an element-pleiad (K. Fajans, 1913). On the other hand it is observed in some instances that different elements have atoms of identical mass, but of different atomic numbers: these kinds of atoms are called isobares. Isobares exhibit unlike chemical properties. Thus, the number of different kinds of atoms was found to be much greater than ninety-two.

Atoms and ions, being chemically undecomposable and forming all substances, are, according to definition, elements. At the present time some three hundred different kinds of atoms are known. Each of them can produce several ions, so that the total number of these elements, different atoms and ions, approximates one thousand. It is easy, however, to systematize them: ions are directly connected with atoms, being, in fact, formed from atoms by addition or by elimination of electrons, and having acquired in consequence an electrical charge. Thus, only atoms have to be classified by means of their atomic numbers. Each group of atoms and their ions having the same atomic number form one aggregation. Each such aggregation is *one chemical element*, which can be defined thus: *a chemical element is a principle, all atoms and ions of which have the same atomic number.* This definition is based on the resolutions passed by the International Union in 1923. Chemical elements can be divided into homogeneous (all atoms are of an identical mass), and heterogeneous (having several kinds of atoms differring by their mass, *i. e.*, consisting of several isotopes), as I have called the "simple" and "complex" elements of the International Union (the ultimate component parts of course cannot be "complex" by the very nature of things).

The chemical atomic weight of an element, *i. e.*, the value of its equivalent mutiplied by the valency, expresses the mean weight of an enormous number of atoms of a given principle. The physical atomic weight is calculated from the mass of atom of each isotope and from the relative abundance of these isotopes. At the present time these two atomic weights practically coincide for all chemical elements (principles), where both can be determined.

Atoms and ions are themselves built up of protons, neutrons, electrons, etc.; of course, these are also elements, but not chemical ones: the chemical analysis does not go beyond atoms and ions. These constituent parts of atoms and ions, determined by physical analysis, may be called ultrachemical elements.

MIDWEST REGIONAL MEETING OF THE A. C. S.

The Midwest Regional Meeting of the American Chemical Society will convene in Omaha, Nebraska, on Thursday, April 29, Friday, April 30, and the forenoon of Saturday, May 1, 1937. All meetings will be held in conveniently located and air-conditioned rooms on the mezzanine floor of the Hotel Paxton in downtown Omaha.

Divisional groups have been organized as follows:

1. Dr. Frank B. Dains, University of Kansas, chairman of the chemical education and history of chemistry group. Secretary, Dr. Arthur W. Davidson, University of Kansas, Lawrence, Kansas.
2. Dr. M. J. Blish, University of Nebraska, chairman of the agricultural and food chemistry group, Experiment Station, University of Nebraska. Secretary, Dr. G. F. Stewart, Omaha Cold Storage Company, Omaha. This group is organizing a symposium on "Eggs."
3. Dr. Edward Bartow, University of Iowa, chairman of the industrial chemistry group. Secretary, Dr. L. B. Parsons, Cudahy Packing Company, South Omaha, Nebraska.
4. Dr. Cliff S. Hamilton, University of Nebraska, chairman of the organic chemistry group. Secretary, Dr. Mary L. Morse, Duchesne College, Omaha.
5. Dr. L. F. Yntema, University of St. Louis, chairman of the physical and inorganic group. Secretary, Dr. E. Roger Washburn, University of Nebraska.

Titles are invited and should reach the respective group secretaries not later than March 13.

EARLY CHEMICAL LABORATORIES WEST *of the* MISSISSIPPI*

HARRISON HALE

University of Arkansas, Fayetteville, Arkansas

"A REPORT on the Teaching of Chemistry and Physics in the United States," by Frank Wigglesworth Clarke, Circular of Information, No. 6-1880 of the United States Bureau of Education, is a mine of valuable information. Although the paper was written while the author was a young man, some twenty years before he became president of the American Chemical Society, it is distinguished by its content, as well as by its clarity of expression.

In writing more than half a century ago of the teaching of chemistry in the United States, he says (*1*), "By slow degrees the study of chemistry was introduced into American medical schools and colleges. In the former class of institutions it was taught at first in connection with materia medica. The University of Pennsylvania Medical school in 1768, the medical school of Harvard College in 1782, and the Dartmouth school in 1798 are among the places at which the science was early recognized. The colleges proper were perhaps somewhat slower in extending their hospitality to the new branch of learning. At William and Mary there was a professor of chemistry and natural philosophy as early as 1774; but Princeton was the first academic college to award to chemistry the honor of a separate chair. Here, in 1795, Dr. John Maclean became professor of chemistry, but at a later period the labor of instruction in mathematics and physics was also assumed by him. The lead thus taken was followed by Columbia College in 1802; by Yale, in 1803; by Bowdoin, in 1805; by South Carolina College and Dickinson College, in 1811, and so on by college after college until chemistry was recognized as an important branch of study all over the land."

All of these institutions are near the Atlantic Coast. It occurred to me that in this meeting here, in what its citizens called "The Heart of America," it would be fitting for this Division to consider the subject of early chemical laboratories west of the Mississippi. I thought that possibly the University of Arkansas, with which I am associated, might be in this group since it has offered laboratory instruction in chemistry continuously for sixty-four years, ever since it was founded in 1872. Investigation revealed, however, some institutions which were offering such instruction before 1830.

Thus, in the preparation of this brief paper, there have been included only those laboratories which were in operation before 1860. This antedates two mighty forces, the one cataclysmic and destructive, the Civil War; the other working quietly but effectively, the land grant college. Of this second force Clarke writes (*1*), "In the year 1862 an event happened the full importance of which has not yet been generally understood. It was during the darkest period of the civil war that Congress, notwithstanding the excitement due to current events, in spite of the pressure of affairs involving the very life of the nation, found time to pass an act granting to the several states large areas of public lands for the endowment of agricultural and mechanical colleges. After the war had ended, the seed thus generously planted began to grow. In some states the land grant went to strengthen old institutions, in others it founded new schools; but in every instance it was the modern scientific education that reaped the greatest benefit. . . . In short, the national land grant not only fulfilled the purpose for which it was originally intended, but it also gave to scientific education the greatest stimulus which the latter ever received upon this continent."

One might wonder if in 1860 there were any chemical laboratories west of the Mississippi River, for there were only eight states in the region, two newly admitted to the Union: Louisiana admitted in 1812, Missouri in 1821, Arkansas in 1836, Texas in 1845, Iowa in 1846, California in 1850, Minnesota in 1858, and Oregon in 1859. In all that vast territory there were less than twenty towns of five thousand people (*2*).

In spite of this small and widely scattered population some thirty-five colleges were in the region. Of these Minnesota had only one, while Iowa had nine. Missouri had seven, Arkansas two, Louisiana six, Texas three, Oregon three, California three (*3*). Most of these were not state institutions. Here it was true as stated last November in an address by President Bizzell of the University of Oklahoma (*4*), "The church colleges, as a general thing, were the first institutions of higher education to be established."

Of the original group of colleges west of the Mississippi some are not in existence now and not all offered instruction in chemistry. The year in which such instruction was begun in each institution is usually stated by Clarke, but just how much laboratory work was done is not known. The date of founding of each institution is taken from Colleges and Universities in the Encyclopedia Americana, 1935 (*5*), checked against the World Almanac for 1936 (*6*). Frequently actual instruction did not begin until some years later.

* Presented before the Division of Chemical Education at the Kansas City meeting of the A. C. S., April 14, 1936.

EARLY CHEMICAL LABORATORIES WEST OF THE MISSISSIPPI

Institution	*Dates of founding*	*Dates of actual instruction*	*Dates of appointments of first chemistry teachers*	*First chemistry teacher*	*Textbook used*	*Source of information*	*Source of information given by*
St. Louis University	1818	1818	1831, 1827	P. J. Verhaegen		Catalogs	J. P. Coony
Centenary College	1825	1825	1829, 1830	Lt. H. H. Gird Dr. Ingles		Reports of Faculty, Board of Trustees	John B. Entrikin
University of Missouri	1839	1842	1842, 1840	Edward H. Leffingwell	Johnston, "Chemistry"	Catalogs, History of Boone County	Lloyd B. Thomas
Southwestern University	1840	1841	1841	Rev. C. W. Thomas	Johnston (Turner), "Chemistry"	Catalog	J. C. Godbey
Baylor University	1845	1846	1851	Rev. J. B. Stiteler	Johnston (Turner), "Chemistry"	Catalog, Diamond Jubilee Transactions of Faculty Studies	E. W. McDiarmid, Jr., Librarian
Grinnell College	1846	1848	1853, 1850	D. S. Sheldon Rev. Henry W. Bullen	Silliman, "Chemistry"	Catalogs	Leo P. Sherman
Tulane University of Louisiana	1834	1834	1834	Medical, T. R. Ingalls	Noad's "Analytical Chemistry"	Catalogs	H. W. Moseley
	1834	1834	1853	Academic, J. L. Riddell and W. P. Riddell	Rose's "Chemical Analysis"	Historical Documents	H. W. Moseley
Austin College	1849	1850	1853	Rev. A. E. Thom	Turner, "Chemistry"	Catalog, Minutes of the Board	P. S. Wharton
Pacific University	1848	1848	1854	President S. H. Marsh		Minute Books, Historical Bulletin	Francis T. Jones
Cornell College	1853	1854	1854	S. N. Fellows	Youman's "Chemistry"	Catalogs	J. B. Culbertson
Iowa Wesleyan College	1842		1854	Rev. George C. Whitlock	Johnston (Turner), "Chemistry"	Catalogs	Martha Doan
State University of Iowa	1847	1855	1855	Josiah D. Whitney		Catalogs, Article in "The Chemist"	Edward Bartow
College of the Pacific	1851		1856	Professor Draper			A. T. Bawden
Washington University	1853	1854	1858	Abram Litton, M.D.		Catalogs, Records of Board, the Historical Documents	Holmes Smith

Notices of corrections or additions sent to Harrison Hale, University of Arkansas, Fayetteville, will be appreciated.

In the group of earlier chemical laboratories we would include fourteen, although we realize that this list is probably not complete nor entirely accurate. Additions and corrections are invited. In every case we have checked these statements by personal correspondence with present-day teachers of chemistry to whom we are very much indebted (*7–20*). In considering data which were generously supplied by other teachers we have found that certain early institutions did not teach chemistry before 1860.

St. Louis University seems to have been the oldest of these colleges and universities and the first to teach chemistry. It was founded in 1818, actual instruction beginning in that year. Clarke states chemistry was first taught there in 1827. Professor Coony reports 1831 "probably the earliest" with P. J. Verhaegen as teacher. There were lecture demonstrations, but no laboratory instruction at first. " 'Natural Philosophy' was the title of what we call 'Science Courses' and included Physics, Chemistry, Geology, Botany, Mineralogy (*7*)."

Centenary College of Louisiana, located at Shreveport since 1908, was founded at Jackson (just east of the Mississippi River) in 1825. Lt. H. H. Gird, a graduate of West Point, is reported to have taught chemistry in 1829. The next year Dr. Ingles, also from West Point, was professor of chemistry and natural philosophy (*8*).

According to Clarke, the University of Missouri at Columbia, founded in 1839, with the first teaching of chemistry in 1840, seems to come third. According to another report, the junior class studied chemistry and natural philosophy in 1842. The senior class had lectures on natural philosophy and chemistry, and the lectures were demonstrated by use of apparatus. Edward H. Leffingwell was the teacher; Johnston's "Chemistry" was reported as in use in 1844 (*9*).

Ruterville College, at Ruterville, Texas (Southwestern University at Georgetown, Texas, since 1872), was founded in 1840. Chemistry was taught by Rev. C. W. Thomas in 1841, the first year of instruction. Johnston's (Turner's) "Chemistry" was used, probably without laboratory work (*10*).

In Baylor University founded in 1845, at Independence, Texas, Rev. J. B. Stiteler taught chemistry in 1851 in the junior year using Johnston's (Turner's) text. Laboratory work did not come till later (*11*). Baylor has been at Waco since 1868.

In 1850 in Iowa College at Davenport, now Grinnell College at Grinnell, Iowa, Silliman's "Chemistry" was taught in the senior year by Rev. Henry W. Bullen, Professor of Mathematics and Natural Philosophy. D. S. Sheldon, Professor of Chemistry and Natural Sciences, taught there in 1853 (*12*).

In the Medical College of Louisiana, T. R. Ingalls taught chemistry in the year of its founding, 1834. This became the medical department of what is now known as the Tulane University of Louisiana at New Orleans in 1847. In the academic department of this university, chemistry was first taught in 1853 by J. L. and W. P. Riddell, using Noad's "Analytical Chemistry" and Rose's "Chemical Analysis (*13*)."

As an interesting digression, it is worthy of note that the College of Technology of Tulane offered courses in Chemical Engineering in 1894 and awarded the Ch.E. degree in 1896. It is thought that this was "the very first in this part of the country, if not in the whole country (*13*)."

In 1853, also, chemistry was taught in Austin College, Sherman, Texas, by Rev. A. E. Thom, the course being described as "Chemistry with Experiments." Turner's "Chemistry" was the text in 1857 (*14*).

Of the eight institutions that seem to have been the first to teach chemistry, seven were south of an east and west line through Kansas City. The ninth apparently was in Oregon which was admitted to the Union in 1859. At Pacific University in Forest Grove, President S. H. Marsh, Professor of Languages and General Science, taught chemistry about 1854. Many old chemistry texts of that period are still in the university library. "The original lab still is used although the Chemistry Department occupies the whole building. (The oldest west of the Rockies still used for educational purposes—hand-hewn timbers, joints mortised and pegged with wooden pegs.) Same old apparatus still in laboratory: large retorts, receivers, balances, sets of weights, specific gravity floats, etc. Building still heated by wood-burning stoves (*15*)."

In the same year, 1854, chemistry was taught for the first time in two Iowa institutions. At Cornell College in Mt. Vernon, S. N. Fellows used Youman's text in the first year in which instruction was given in the college (*16*). At Iowa Wesleyan in Mt. Pleasant, George C. Whitlock, Professor of Mathematics and Natural Science, used Johnston's text. Chemistry is listed in the catalog of 1854 as a subject for the junior class. "First term, chemistry commenced; second term, chemistry finished (*17*)."

The State University of Iowa at Iowa City seems to have been the second state institution west of the Mississippi to teach chemistry. This was in 1855, the first year in which instruction was given; Josiah D. Whitney was professor of chemistry. According to the first circular (September, 1855), "The Department of Chemistry is to embrace analytical and elementary chemistry, both inorganic and organic, with its application to agriculture and the arts (*18*)."

Professor Draper is reported to have taught chemistry in 1856–57 in the College of the Pacific at Stockton, California (*19*).

In Washington University, St. Louis, Missouri, chemistry was first taught January 1, 1858, by Abram Litton, M.D., and included laboratory work. The Chemical Laboratory, second building of Washington University, Washington Avenue and St. Charles Street, was finished in 1858 (*20*).

It is interesting that nearly a third of these laboratories were in Iowa, which was not admitted as a state till 1846. Parker's "Higher Education in Iowa" shows how difficult the educational situation was and how uncertain exact dates and statements may be (*21*).

Clarke lists one hundred seventeen "Textbooks relating to Physics" and two hundred eleven "to Chemistry" in use about 1880. Of these, eighty-seven are classified as general chemistry, thirty-five qualitative analysis, but only seven as organic chemistry. Many of these were written abroad. The list of foreign authors includes some distinguished names, such as Frankland, Graham, Regnault, Roscoe, Thorpe, Wurtz, Wöhler, Beilstein, Clowes, Fresenius, and Muir, while some of the prominent American authors given are Barker, Bloxam, Caldwell, Cooke, Draper, Eliot, Nason, Silliman, Crafts, Prescott, Remsen, and Wiley. Under the classification general chemistry are included "Johnston, J., Elements of Chemistry, Philadelphia, Desilver" and "Johnston, J., Manual of Chemistry on basis of E. Turner's elements," with the same publisher. These seem to have been widely used.

So far as we have been able to learn, there were no commercial laboratories in St. Louis in this early period (*22*). In closing, a statement made by Clarke is worth quoting because of questions which arise today: "For school purposes, ten thousand dollars' worth of appliances for showing lecture experiments is of less real value than a good laboratory outfit accessible to students and costing but one-twentieth of the sum (*23*)."

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SOME DEVICES *for* COMBATING "VERBALISM" *in the* TEACHING *of* ELEMENTARY CHEMISTRY*

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"VERBALISM" may be defined as the more or less accurate reproduction, by the student, of the words of the text, without any satisfactory comprehension of its meaning.

Classical education consisted largely of sheer memory work. The older teachers assumed—unconsciously, perhaps—that if the student memorized the text and repeated it with sufficient pertinacity, some faint glimmer of its significance would dawn in his mind. "*Repetitio mater studiorum est.*" If the student did not possess sufficient intuition to grasp the meaning of a plain, logical statement, he was not worth educating. The field of learning was relatively narrow, and there was time for endless repetition and long meditation. As a rule, moreover, only a small proportion of the best minds were subjected to the formal educational process. Much might be said for the classical policy, and for the classical method. In a few cases it produced outstanding results. The educational ideal of our age, however, is not merely to educate everybody, but to give as broad and comprehensive education as possible in the least practicable time and with a minimum of exertion on the student's part. Some other technic is obviously indicated.

In modern scientific courses the hapless student, usually of mediocre ability, is plunged without warning into a mass of facts, definitions, and philosophical propositions which the best minds of the human race required centuries, or millennia, to elucidate. His commonest resource, in the face of this emergency, is to retire to his room, bone the words into his brain overnight, and regurgitate them, more or less hopefully, in quiz or examination the next day, trusting to luck that he may have guessed the words or phrases that the teacher wanted.

One of the oldest devices to detect such unintelligent verbalism is to require the student to reproduce the subject matter "in his own words." This plan worked fairly well as long as the high schools were able to give their students adequate courses in composition, precis-writing, vocabulary-building, etc. Of late years, however, English has been crowded out of high-school curricula to such an extent by the introduction of other branches and activities that the average high-school graduate hardly knows what you mean when you ask him to say anything in his own words. He wonders why the words of the text aren't good enough for the teacher. Too often he is in the position of the student who remarked that he would do very well in composition but for two slight difficulties: he had no thoughts to express, and no words to express them with. This method, therefore, usually breaks down, under modern conditions. The wise teacher, however, will never discourage the rare student who tries to express himself in his own words. However incoherent, jumbled, and chaotic the student's first wavering steps in self-expression may be, the intelligent teacher will welcome enthusiastically the faintest indication that the student is actually trying to think for himself. Any student, nowadays, who succeeds in giving the correct meaning of the text in his own words should be given an "A" with a double "plus."

Since Sir John Adam's pioneer work on "illustration," the art of illustration in exposition has been enormously developed. Educational textbooks and individual teachers have shown great industry and ingenuity in discovering so many illustrations that one student plaintively remarked, "Everything seems to illustrate everything else," an observation the philosophical profundity of which, however unintentional, is not to be lightly ignored. My suggestion on this point is that teachers should not be too fecund with illustrations, but should encourage students to find their own illustrations. Go around the class and ask each student to suggest some illustration, from common knowledge and

* Presented before the Division of Chemical Education at the ninety-first meeting of the American Chemical Society, Kansas City, April 15, 1936.

experience, of the law or principle under consideration. An examination of the illustrations thus offered will usually betray very clearly whether or not the student has grasped the idea.

During the past few years there has been a constantly increasing recognition of the quantitative nature of all genuine science. No generalization regarding natural phenomena is regarded as truly scientific unless it can be mathematically stated. No student should try to deceive himself into thinking that he understands a scentific law until he masters its mathematical application and can work problems which illustrate it. These considerations have led to the wide use of problems in science teaching. Ability to work problems has come to be judged the best test of the student's comprehension. Yet here, again, extensive verbalism has crept in. Teachers and textbook writers alike have fallen into the assumption that the average student understands an algebraic derivation. If, with the aid of a supplied formula, the student can work problems, his grasp of the principles involved is taken for granted. This, of course, is nonsense. It is easy to show students how to substitute figures for the letters of a formula and "cancel out" without the student's obtaining the slightest idea concerning the realities for which the figures are supposed to stand. Save as an exercise in arithmetical operations, this is perhaps one of the most futile teaching technics that has ever been devised. Students frequently attain great facility in "balancing chemical equations" without ever catching a glimpse of the notion that these symbolical expressions represent things that actually happen.

Formulas are the tools of technicians and, in the hands of masters, of research. It is not often that formulas can be profitably used in teaching elementary sciences. Not one elementary chemistry student in a hundred will ever be required, for practical purposes, to calculate the effect of given changes of temperature and pressure upon a given volume of gas. But it is extremely important that the student should get the general idea of these changes, and the fact that they can be accurately predicted, thus being led toward the concept of the universal kinetic nature of matter. "Gas-law problems" will therefore doubtless continue to be an essential part of introductory chemistry courses although, as commonly presented, they constitute one of the most formidable obstacles in the path of the beginning student.

The best resource against verbalism is the cultivation of the student's scientific imagination—getting him to visualize in a concrete way every problem he attacks. Taking the gas-laws as an example, it should hardly be necessary to suggest that the student's first exercise should be the preparation of several samples of different gases, the measurement of their volumes, and the actual demonstration of the volumetric changes consequent upon alterations of temperature and pressure. When it comes to problems, each law should be presented separately, without reference to the others. Instead of providing the student with a formula, the teacher should ask the student to think for himself, and decide whether the change of conditions described by the problem will increase or decrease the volume in question. The student, if he has mastered the "rule of three" (an unjustifiable assumption in most cases), will then be able to arrange his proportion according to common sense. If he finds proportions baffling—which is usually the case—he can simply multiply his original volume directly by the ratio of pressures, or temperatures. He has already decided, by means of a practical, common-sense inspection of the problem, whether the volume will increase or decrease. It may be necessary to explain to him that multiplication by a proper fraction will decrease the original value, etc. Having seen his way through the problem from the beginning, the details of arithmetical manipulation will be incidental, as they should be. Also, an inspection of his answer when obtained, will usually tell him whether or not he has made any serious mistakes in calculation.

After the laws of Charles and Boyle have been presented separately, "combined" problems may be taken up. Here, however, instead of giving the student the formula: $\frac{VP}{T_a} = \frac{V'P'}{T_a'}$, the student should be taught to set down the known volume (in the most common type) and then consider successively what effect the temperature change will have on this volume, and then the effect of the pressure change. This procedure should enable him to see his way intelligently through the problem and anticipate, approximately, what his answer should be.

A more searching test of the student's comprehension is to reserve certain types of problems for quiz and examination purposes. If, for example, the student has been properly taught how to calculate the effects upon volume of temperature and pressure changes, and the effects upon temperature of pressure and volume changes, he should be able, on his own, to figure out the effects upon pressure of temperature and volume changes. If, upon being presented with a new type of problem, he objects that he has never been shown how to do that kind of example, it is a sure sign that he has not understood the matter in any fundamental way.

The use of "contracted methods" of multiplication and division can be a real aid in preventing verbalism. Very few elementary chemistry students can use slide-rule or logarithmic methods with any certainty, and most of them welcome the contracted methods as something like magic. In the first place, they can be so taught as to compel the student to "throw away" the decimal point at the outset. He must then visualize his problem concretely in order to decide where to put it when he has worked out the numerals of his answer. Not only is the method a great time-saver, but it leads students away from the illusion that if they carry out all problems to the bitter end of the eleventh decimal place, they are doing something worthwhile. It may help them to see that arithmetic is merely a tool, and should not be a stumbling-block. The diligent but

unintelligent student often tries to arouse his instructor's compassion by presenting voluminous calculations, most of which have no real meaning.

Care should be taken, of course, to show the student that contracted methods are not "sloppy"—that, on account of the limitations of observational accuracy, they are really far more scientific than long-winded calculations based upon the assumption of an accuracy that is actually unattainable in real laboratory measurements. Students should be trained to think of the problem rather than the method. It is a common experience for the student to become so lost in a maze of complicated and superfluous calculations that long before he gets through with the problem he has entirely forgotten what it was all about. Some teachers penalize the students who carry out their calculations to more decimal places than is justified by the accuracy of the observations upon which the problem is based.

The final test of a student's fundamental comprehension of chemical theories lies in his ability to work "synthetic" or "cross-country" problems, *i. e.*, problems which involve two or more related laws or principles. It should hardly be necessary to point out that the successful working of such problems does not constitute a valid test if the teacher has already presented all possible types and, perhaps, has furnished formulas for their solution. It should suffice for the teacher to point out the relationships between the various laws and work through a few problems, always leaving some types in reserve with which to prove the student's original ability. Most texts, for example, do not give the simple derivation of Graham's law of gaseous diffusion from the kinetic equation: $PV = \frac{1}{3} mnu^2$. This can be assigned as a problem, after explaining the stock derivation of Avogardo's hypothesis.

A few suggestive "synthetic" problems are appended.

1. "Avogadro's number" is given as approximately 6×10^{23}. How many molecules would one liter of gas at 27°C. and 750 mm. pressure contain?

2. Two oxides of sulfur contain, respectively, 50 per cent. and 60 per cent. of oxygen, by weight. Use these data to illustrate the law of multiple proportions.

3. Twenty-five cc. of oxygen and fifty cc. of hydrogen, originally at 27°C. and normal atmospheric pressure, are exploded in a eudiometer tube. After the explosion the temperature of the gases is found to be 177°C. and the volume seventy-five cc., at atmospheric pressure. Show that these data are in harmony with Gay-Lussac's law of volumes.

4. Two-tenths gram of a non-electrolytic organic substance, when vaporized in a Victor Meyer apparatus, is found to occupy 45 cc. at 20°C. and 740 mm. pressure. Calculate the freezing point of a two per cent. solution of this substance. (In water.)

5. A bottle of "soda-water" which was charged with CO_2 at three atmospheres pressure is opened at a pressure of one atmosphere, the temperature being 18°C. and gives off 500 cc. of CO_2. What further weight of CO_2 will be given off if the open bottle is placed in a vacuum?

6. At 950°C. hydrogen iodide dissociates to the extent of two thirds into free hydrogen and free iodine. If there is added to this system sufficient hydrogen to double the amount of free hydrogen originally present, what will be the final concentrations of the gases present, at equilibrium?

7. The specific resistance of a two per cent. solution of ferric sulfate in water, at 18°C., is 80 ohms. The specific resistance of a 0.001 per cent. solution of the same salt is 100,000 ohms. Assume complete dissociation in the case of the latter solution and calculate the freezing point of the two per cent. solution.

8. A pan of water at 15°C. is placed on a stove which gives off heat at a constant rate. The water begins to boil after twenty minutes. How long will it take the water to boil dry?

NOTE ON CONTRACTED ARITHMETICAL METHODS

According to Cantor (*Geschichte der Mathematik*, Vol. II, p. 567) Joost Bürgi (1552–1632) first introduced "contracted" methods of multiplication. The theory of these methods is given in several American textbooks, *e. g.*, Whitaker's "Elements of Trigonometry" (pp. 8–10) and Garabedian and Winston's "Plane Trigonometry" (pp. 59–65). Most European textbooks of secondary mathematics present these methods and provide extensive exercises in working problems to any required degree of accuracy. It is important to emphasize the fact that most physico-chemical observations do not have an accuracy which justifies the carrying out of the calculations to more than four significant figures.

As an example of a "simplified" method recommended for elementary chemistry courses a typical "gas-law" problem is chosen.

Problem: A volume of gas is measured to be 45.25 cc. at 23.5°C. and 635.2 mm. pressure. What volume would this gas occupy at 18.3°C. and 755.6 mm. pressure?

Analyzed by the "common sense" method this problem assumes the form: Required volume $= \frac{45.25 \times 291.3 \times 635.2}{296.5 \times 755.6}$ cc.

The average student, using common arithmetic, will fight this out to the bitter end, putting down at least two hundred digits, and arriving finally at some such answer as 37.36359+, the last three or four figures of which have no possible real meaning. The work by contracted methods, to three significant figures, is as follows.

4525	1318	2965	37.3
2913	6352	7556	224÷837
——	——	——	672
905	791	2716	——
407	39	148	165
5	7	15	157
1	——	1	——
——	837	——	8
1318		2240	7
			——

The decimal point is easily determined by intelligent inspection of the original data of the problem.

QUALITATIVE ANALYSIS *as a* PART *of the* ELEMENTARY ORGANIC LABORATORY COURSE

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During the past four years at Yale University the authors have been developing a new type of laboratory work for the elementary organic chemistry course. This involves the introduction of experiments upon the identification of unknown organic substances, presented in a more simple manner than is the case in the ordinary course in qualitative organic analysis. This type of work is substituted for one-half of the preparations formerly done.

The results have been highly satisfactory. The students enjoy the laboratory work more, and learn more chemistry and a laboratory technic ordinarily missed.

This paper outlines the method of presenting this new laboratory course.

✦ ✦ ✦ ✦ ✦ ✦

THERE are two important reasons for giving laboratory work in connection with courses in elementary organic chemistry. In the first place, it is quite impossible for a student to obtain anything but the most trivial acquaintance with organic laboratory technic without working in the laboratory himself. In the second place, the material studied in the classroom becomes much more real to the student when he is given an opportunity to apply it to actual cases in the laboratory.

The authors have for some time been dissatisfied with the effectiveness with which the usual course in preparations given in the elementary organic laboratory meets these two objectives. The points of preparative technic with which it is important that the student become familiar in the elementary course are comparatively few in number, and furthermore it is not essential for him to become really expert in these operations. If he is majoring in chemistry there will be sufficient opportunity for this in his later courses, and if his major interests lie in some other field it is foolish for him to spend the time necessary for the acquirement of such manual expertness. For these reasons the authors are convinced that a full year of preparation involves an amount of repetition of laboratory operations which is unnecessary for students the majority of whom will not go on further with chemistry. If the preparations are selected with the purpose in mind of including a comparatively wide variety of methods, both chemical and manual, it is perfectly possible for the student to obtain a sufficient amount of preparative technic during one semester in a course which includes four to six hours of laboratory work per week.

The preparative work in the elementary organic laboratory is only too apt to develop into so-called "cookbook" chemistry unless the student's interest in what he is doing can be maintained at a rather high level. This situation becomes particularly serious after the novelty of the new laboratory methods has worn off and the student finds he is expected to keep on all year making compound after compound, using essentially the same methods of recrystallization, distillation, extraction, and so on. We freely admit that these remarks do not apply to the student who becomes really absorbed in organic chemistry, but we are convinced that they do apply to the majority of students of the subject. The logical way to avoid this development would seem to be to anticipate it by a radical change in the type of laboratory work after the first semester.

A third objection to the usual course of preparations, and the one which is probably the most important for the majority of students, is that such a course is comparatively inefficient in accomplishing the second objective of elementary organic laboratory work mentioned above, namely, that of giving the student what might be called first-hand contact with the reactions studied in the classroom. The purely manual aspects of the preparation of organic compounds are so time-consuming that the student gets a chance to actually observe only a very small number of reactions.

For some years there has been an increasing amount of attention given to the inclusion of qualitative organic analysis in the training of chemists, particularly organic chemists. Recognizing this important trend, and believing that qualitative organic analysis has as great pedagogical value as qualitative inorganic analysis, the authors decided four years ago to try the experiment of replacing the second semester of preparations in the elementary course by qualitative analysis. So far as we are aware, laboratory courses in this subject have always been given after the elementary course in organic

chemistry and have thus been considered as advanced courses taken only by chemistry majors.

It seemed to be necessary to present this type of laboratory work in a form somewhat more simplified than that usually employed in more advanced courses. We therefore selected a group of about 150 common organic compounds and devised a system for their qualitative identification. This system is based on the same general principles and methods as the more comprehensive systems such as that of Mulliken, but, wherever possible, use has been made of chemical rather than physical properties. We have extended the list of compounds included in the system each year until at present some 300–400 are included. It is to be emphasized that we have not attempted to devise a comprehensive analytical system. We have been interested in the qualitative analytical work mainly as a pedagogical tool, and at the same time have attempted to show the student, in a general, rather than detailed, manner, the principles and methods involved in qualitative organic analysis.

In proceeding with the identification of an unknown substance the student must first discover and apply a suitable method of purification.* In doing this he will in most cases also determine the melting or boiling point of the compound. He then performs the usual qualitative elementary analysis. The preliminary identification of the unknown is accomplished by the systematic application of special tests. At present we are using thirty-two of these tests, a few of which are specific for one substance, and only one of which, a test for solubility in water, involves what might be called a physical property. Obviously, only a few of these tests need to be applied in any given case. A few quantitative procedures, namely the determination of densities and neutralization and saponification equivalents, have been included.

We have constructed a key to guide the student in his application of the special tests. This appeared to be necessary because of the anomalous reactions of many of the compounds to the special tests. For example, the student is taught in the classroom that bromine will add to a carbon–carbon double bond; as a matter of fact, in chloroform solution maleic and fumaric acids remain apparently unaffected by this reagent after a reasonable length of time. Cases of this kind make it difficult for the student to rely exclusively on the information he has received in the classroom. However, we believe that if the student is required to include in his notebook equations for all the tests performed, he will become familiar with certain features of organic chemistry which would otherwise be missed. A sample of the key is given, with explanations of the tests involved.

* In this elementary course we believe it to be advisable to inform the student if his unknown is one which cannot be readily purified. Much time is thus saved which would otherwise be wasted in vain attempts to purify such substances as proteins, sugars, or other compounds having properties such as high solubility or instability which render purification too difficult for elementary students.

ORDER I.—GROUP C†

Apply test 2.

I. Test 2 positive. Indicates an acid or acid anhydride. Apply test 3b.

1. Test 3b positive.

B.P.

101 Formic acid. Sharp odor. Tests 3a and 22 pos.

dec. Lactic acid. Thick sirup boiling with decomposition. Tests 3a neg., 12 pos.

2. Tests 3a and 3b negative.

B.P.

118 Acetic acid. Sharp odor. Solidifies in an ice bath.

139 Acetic anhydride. Sharp odor.

141 Propionic acid. Sharp odor. Does not solidify in ice bath.

163 *n*-Butyric acid. Rancid odor.

168 Propionic anhydride.

II. Test 2 negative. Apply test 6.

1. Test 6 positive.

B.P.

21 Acetaldehyde. Tests 7a, 10, 11, 12 pos.

50 Propionaldehyde. Tests 7a, 10, 11 pos., 12 neg.

56 Acetone. Tests 7a, 10, 11 neg., 12 pos.

73 *n*-Butyraldehyde. Tests 7a, 10, 11 pos., 12 neg.

81 Butanone. Tests 7a, 10, 11, 13 neg., 12 pos.

103 Crotonaldehyde. Tests 7a, 10, 11 pos., 12 neg.

155 Cyclohexanone. Tests 7a, 10, 11, 12 neg.

161d. Furfuraldehyde. Tests 7a, 9, 10 pos., 12 neg.

2. Test 6 negative. Apply test 13.

a. Test 13 positive.

B.P.

66 Methyl alcohol. Test 12 neg.

78 Ethyl alcohol. Test 12 pos.

83 Isopropyl alcohol. Test 12 pos. in the cold.

97 *n*-Propyl alcohol. Test 12 neg.

The student is required to verify his preliminary identification by the preparation of a crystalline derivative wherever this is reasonably possible. Included in the mimeographed sheets supplied to the student is a section on the preparation of derivatives. Various types of derivatives are suggested for each class of compounds, directions (in general form wherever possible) are given for their preparation, and the appropriate melting points are listed. Thus in nearly all cases the student will find that he has to choose between several possible derivatives for his compound; in this way he is not only required to study some fundamental organic chemistry, but he has to consider it closely enough to decide which derivative prepara-

† Order I includes all compounds containing no halogen, nitrogen, or sulfur. Group C is composed of the liquid, water-soluble members of Order I. Test 2 involves liberation of carbon dioxide from sodium bicarbonate in the presence of an acid or acid anhydride. Tests 3a and 3b are modifications of the von Baeyer permanganate test. Test 22 involves reduction of aqueous mercuric chloride. Test 12 is the iodoform reaction. The reagent for test 6 is a solution of bromine in carbon tetrachloride. Test 7a is a modification of Fehling's test, 10 is the test with Tollen's reagent, 11 is Schiff's aldehyde test, 13 is a test for compounds containing groups which react readily with acetyl chloride, and 9 is the orcinol test for pentoses (furfuraldehyde).

tion will be most suited to his particular requirements.

It has been our experience that each unknown requires on the average about five hours for identification and preparation of a derivative. This time, of course, varies greatly with the nature of the unknown, the ease of purification being one of the chief controlling factors. It is thus difficult to set a definite requirement for a class in terms of the number of unknowns which must be completed. It is desirable to assign each student unknowns illustrating a variety of classes of compounds, and to distribute the assignments about evenly between solid and liquid unknowns. Some of the better students are assigned one or two unknown mixtures. This type of work introduces the additional problem of separation.

It has been our observation during the four years of its trial that this method of teaching has been even more successful than we had hoped. Some of the advantages obtained from this change in laboratory work will be discussed.

Of great importance is the fact that most of the students (about 450 have taken the course so far) enjoy the qualitative work much more than they would have enjoyed a second semester of preparations. It goes without saying that they can hardly fail to learn more when they are more interested. They take the assignment of an unknown as much more of a challenge to their ability than the assignment of another routine preparation.

The qualitative work involves an important type of technic which the preparative work does not, namely, the handling of small quantities. In the preparation of derivatives the student is required to start with, depending on the substance, 0.1–1.0 g. of the unknown, and to prepare, purify, and turn in to the instructor an acceptable product. Many of these derivative preparations involve ether extractions, steam distillations, and so on, so that the student must develop good technic to avoid loss of material as a result of poor manipulation.

Finally, it is evident that the student obtains a first-hand experience with a very much wider variety of chemical reactions than would be possible in the same amount of time spent on ordinary preparations. So-called test-tube experiments are included in many elementary organic laboratory courses, but the authors seriously doubt if they are of any real value as usually practiced, since the student has no particular interest in the outcome of the experiment. On the other hand, he will take considerable pains with a test-tube experiment, and will observe the result and consider its significance carefully, if the experiment is involved in the identification of an unknown.

The elementary organic course at Yale includes chemistry majors (in their junior year) and premedical and chemical engineering students. They all do the same sort of work, the chemists having six hours of laboratory per week, while the others have four. The introduction of qualitative analysis into the elementary course has been so successful that in the future qualitative organic analysis will not be given as a separate course at Yale. Qualitative organic analysis rests on certain general principles and involves a limited number of technics which we believe can be absorbed perfectly satisfactorily by the student in his elementary course. The practical aspects of the subject are so detailed in nature and vary so much with the compound being identified that it is doubtful whether anything of value aside from the general principles and technics can be obtained even from a much longer and more difficult course in the subject. As a result of these changes, the chemists will take in their senior year an advanced course in organic chemistry, the laboratory work in which includes preparations and quantitative organic analysis.

It might be of interest to point out that the changes in the laboratory work discussed above have not involved any noteworthy difficulties, aside from the preparation of the mimeographed directions.* The qualitative work involves only apparatus included in the usual set for elementary organic chemistry; the only requirement along this line is a few more test-tubes. A number of reagents are required, but all except two, *p*-bromophenacyl bromide and 2,4-dinitrophenyl-hydrazine, are cheap. It should be pointed out that the expense involved in preparing the reagents is far more than balanced by the saving effected by cutting out a semester of the usual large-scale preparations, which usually yield products of little or no value. It is, of course, unnecessary to have a great many compounds in stock to use for unknowns. As long as the student believes that he may get as an unknown any one of a rather imposing list of compounds it is unnecessary to actually stock a wide variety.

We have found it to be advantageous to alter the usual classroom procedure in order to consider aliphatic and aromatic compounds together right from the start of the year. This order of presentation not only greatly helps the student in the qualitative laboratory work, but it also makes it possible in the preparative laboratory work to rely to a greater extent on aromatic preparations, which are frequently more satisfactory than aliphatic ones involving the same general reactions. We also believe that it is fundamentally desirable to avoid erecting before the student the customary high dividing wall between the aliphatic and aromatic series.

* Since this manuscript was submitted for publication, the mimeographed directions, with some changes, have been published in book form.

A SIMPLE PROCEDURE *for the* DETERMINATION *of the* EQUIVALENT WEIGHT *of* MAGNESIUM

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NEARLY all teachers of chemistry, whether on the secondary-school or college level, believe that a student in elementary chemistry should perform a few quantitative experiments which demand careful experimental technic in order that the student may get some appreciation of the quantitative aspect of the science of chemistry. The determination of the equivalent weight of a metal is a favored experiment to serve this purpose. The equivalent weights of metals such as magnesium, aluminum, and zinc can be determined with a satisfactory degree of precision even by beginning students in chemistry by measuring the volume of hydrogen released under known conditions when a weighed sample of metal reacts with an acid such as hydrochloric acid. There is a tendency to use magnesium for this experiment for a number of reasons:

1. magnesium is readily obtained in a comparatively pure state;
2. the rate of evolution of hydrogen is rapid enough to permit the collection of the hydrogen in a relatively short time;
3. the metal can be obtained in ribbon form, which facilitates the distribution of samples of such weight that they will be sure to release a suitable volume of hydrogen.

That this experiment possesses educational values can be presumed from the fact that procedures for the determination of the equivalent weight of various metals by the displacement method can be found in nearly all high-school and college laboratory manuals in beginning chemistry. This conclusion is further substantiated by the fact that journals dealing with the teaching of chemistry contain many articles outlining various suggestions to make possible greater precision in the value of the equivalent weight as determined by beginning students in chemistry. A very large number of the improvements have been made to get greater precision by making it possible to measure the volume of the displaced hydrogen with greater ease and accuracy.[1]

It is commendable, of course, to make suggestions as to improvement in the technic of this experiment, but the author wishes to point out that many of the suggestions have been more or less futile because of a lack of appreciation of the relative importance of the experimental data that must be collected by the student. The accuracy of the equivalent weight as determined experimentally depends upon four kinds of data:

1. the weight of the metal used;
2. the volume of the hydrogen displaced; and
3. the temperature and the pressure of the hydrogen.

The errors in these data are not of equal significance when considered in the light of their effect of the final value for the equivalent weight. An error of one millimeter in a barometric reading of 750 millimeters cannot affect the final result by more than about 0.1 per cent. The effect of errors in the determination of the temperature are more significant. Let us assume that the temperature of the displaced hydrogen was 20 degrees centigrade and that the error in the determination of this temperature was one degree. The per cent. error in the absolute temperature will be $^1/_{293} \times 100$ or about 0.3 per cent. The probable per cent. error in the volume of the hydrogen will likewise be about 0.3 per cent. with a similar error in the final value of the equivalent weight, or a value of 12.16 ± 0.04, if there were no other errors in the experiment. If, however, the experiment is to be performed carefully enough to demand the use of a eudiometer for the collection of the hydrogen, an ordinary chemical thermometer graduated to degrees is not accurate enough unless it is carefully calibrated. If the error in the volume as read in the eudiometer is assumed to be 0.03 milliliter, the per cent. error in the determination of a volume of 50 milliliters would be 0.06 per cent. This precision would demand that the temperature measurement should be certain to within 0.2 degree (*ca.* 293×0.0006).

The principal source of errors in this experiment, however, is not in the measurement of the temperature and of the pressure. The final result will be much more affected by an error in the *weight of the metal* used in the experiment. Many of the suggested procedures for this experiment imply that the limiting factor in the accuracy possible in the hands of a student is the accuracy with which the volume of hydrogen is measured. This is the usual reason for the performance of the experiment with a eudiometer to collect the hydrogen. In reality, the limiting factor may be, and usually is, the precision with which the sample of metal

[1] *Cf.* SHAH, N. M., J. CHEM. EDUC., **12**, 492 (Oct., 1935). LINCOLN, A. T. AND KLUG, H. P., *ibid.*, **12**, 589 (Dec., 1935).

is weighed. This is easily shown to be the case. For example, 0.04328 gram of magnesium should theoretically displace 45.00 milliliters of hydrogen measured over water at 20°C. and a barometric pressure of 740 mm. If we assume that this volume could be read with an accuracy of 0.05 ml., which corresponds to half of a division on a eudiometer with milliliter divisions, the percentage error in reading the volume would be about 0.10 per cent. The ribbon, then, should be weighed with a comparable order of accuracy, which means that the accuracy should be within ±0.00004 gram (0.04328 × 0.001), which is a degree of precision beyond the range of a high-grade analytical balance. The following table indicates the probable error in the volume of hydrogen that can be expected as a result of errors of increasing magnitude in the weight of the magnesium used in these hypothetical experiments.

TABLE 1

Weight of metal in gram	*Per cent. error in weight*	*Volume of hydrogen over water —20°C. and 740 mm.*[2]	*Probable error in volume of hydrogen*
1. 0.04328 ± 0.00004	± 0.09	45.00 ml.	± 0.04 ml.
2. 0.0433 ± 0.0002	± 0.46	45.0 ml.	± 0.2 ml.
3. 0.043 ± 0.001	± 2.3	45.0 ml.	± 1.0 ml.
4. 0.043 ± 0.003	± 6.9	45.0 ml.	± 3.1 ml.
5. 0.043 ± 0.005	± 11.6	45.0 ml.	± 5.2 ml.

Examination of this table reveals that the limiting factor affecting the final value for the equivalent weight is the accuracy used to determine the weight of the metal. These data also show that effort expended to increase the accuracy of measuring the volume of displaced hydrogen is in most cases wasted effort. Unless the weight of the metal is determined with a precision of 0.2 milligram or less, the use of a eudiometer cannot be justified. If a sample of magnesium, for example, of about 0.040 gram is weighed with a probable percentage error of five per cent. (±0.002 g.), it is not necessary to measure the volume of hydrogen with a precision greater than about 2 milliliters. The precision possible in a volume reading with an ordinary graduate should be better than ±2 milliliters, and this degree of precision should be enough to justify the use of an ordinary graduate rather than a eudiometer to measure the volume of the hydrogen. A possible error of ±5 per cent. in the weight of the metal means, of course, that the final value for the equivalent weight cannot have a precision greater than ±5 per cent., or a value of 12.2 ± 0.6. Values for the equivalent weight varying, then, from 11.6 to 12.8 should be acceptable from the student.

The author has found the following relatively simple procedure to yield satisfactory results in the hands of beginning students. Refer to Figure 1. The beaker has a capacity of 400–600 ml.; (*b*) is a support for the magnesium ribbon made of copper wire of about No. 18 gage. To perform the experiment, the graduate is filled to about one-fifth of its volume with concentrated hydrochloric acid, and then completely filled with cold water. The graduate is then covered with a piece of moist paper (*a*) so as to avoid entrapped bubbles of air. The copper wire support to which is fastened the weighed sample of magnesium ribbon is then placed in the beaker, which previously has been almost filled with cold water. Then, holding the paper (*a*) in place, the graduate is quickly inverted and lowered into the beaker. When the top of the graduate is below the surface of the water, the paper is removed and the graduate lowered over the piece of magnesium. After the reaction is complete, the usual precautions as to the equalization of the temperature, adjusting the water levels to read the volume, etc., should be observed. It is best to use such a quantity of magnesium that the volume of hydrogen set free is not more than two-thirds of the volume of the graduate, to avoid the loss of hydrogen in the form of bubbles from the open end of the graduate. For the same reason, the loop of copper wire with the magnesium should be as far above the open end of the graduate as practicable and still be completely submerged at the conclusion of the experiment. A piece of magnesium ribbon with a weight of about 0.04 gram will set free about the proper amount of hydrogen to collect in a 50-milliliter graduate.

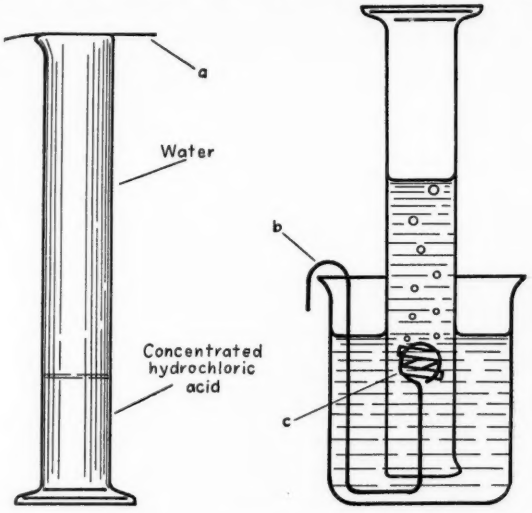

FIGURE 1

This simple procedure, in the experience of the author, gives in the hands of beginning students values for the equivalent weight of magnesium just as satisfactory as those obtained by the use of eudiometers or by some of the more elaborate procedures which involve the determination of the volume of hydrogen by the measurement of the equivalent amount of water displaced by the hydrogen. The student does not need to spend a great deal of time getting ready to perform the experiment, which allows more time for the actual performance of the experiment itself.

SUMMARY

The relative importance of the four kinds of experimental data needed to determine the equivalent weight

[2] The number of zeros after the decimal point indicates the number of significant figures in the volume.

of a metal by the hydrogen displacement method is briefly discussed. It is often true that too much attention is paid to the precise determination of the volume of the hydrogen set free. The degree of precision of the weighing operation of the metal used in the experiment by the average beginning student is usually not very high, so that the value for the equivalent weight in most instances depends almost entirely upon the precision of the weighing operation. Hence, the use of a eudiometer or an elaborate method for measuring the volume of hydrogen displaced is not necessary or justifiable.

DEMONSTRATING THE FIXATION OF NITROGEN

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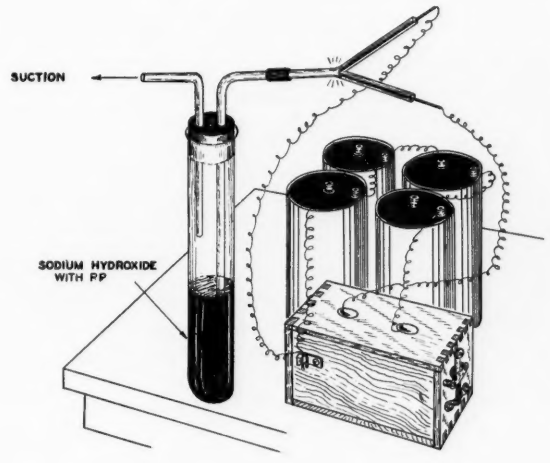
IN THE teaching of the fixation of nitrogen it is very desirable to employ an effective demonstration of one of the methods used in this industry. A simple experiment will motivate the student and give him a better understanding of the principles involved. The arc process lends itself very readily to classroom work, the fundamental equations leading to the formation of nitrogen peroxide and its absorption in water to form nitric acid being easily explained as follows:

$$N_2 + O_2 \longrightarrow 2NO$$
$$2NO + O_2 \longrightarrow 2NO_2$$
$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

If a dilute sodium hydroxide solution is used in place of the water, for the purpose of absorbing the oxide of nitrogen, the formation of the nitric acid can be made more evident. A drop of phenolphthalein imparts to the caustic soda solution a red color, which will shift to colorless when enough nitric acid has been formed to neutralize the alkali present:

$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$

This experiment, which is efficient and easily constructed, and which requires no special apparatus or glass-blowing, may also be used in connection with the study of acids, bases, and neutralization.



APPARATUS

The apparatus is set up as illustrated in the accompanying drawing. The absorption chamber consists of a ten-inch test-tube fitted with a rubber stopper and two bent pieces of glass tubing; the reaction chamber consists of a Y-tube and two stout pieces of copper wire. Four to eight dry cells, connected in series, are attached to an old Ford coil, which serves as an induction coil and boosts the voltage to several thousand volts.

The two wires from the secondary are introduced into the two arms of the Y-tube and act as the electrodes, supplying a good $^1/_4$" arc. The advantage of using a glass Y-tube is that it makes the arc visible to the class. Best results are obtained by sucking a rapid stream of air through the apparatus.

OPERATION

When the apparatus has been arranged, a solution of sodium hydroxide, made up by diluting 5 ml. of a 0.01 *N* sodium hydroxide solution to 50 ml., is colored with phenolphthalein and introduced into the test-tube and the suction is applied. When performed without the use of an arc, the experiment produces no color change and serves to prove that the following changes are not due to the carbon dioxide or other gases in the atmosphere. The air is sucked through the solution for a period of ten minutes.

The experiment is repeated with a second test-tube containing an equal portion of sodium hydroxide solution of the same strength. The arc being used this time, the red alkaline solution turns colorless in approximately ten minutes, demonstrating effectively that nitric acid has been formed from the oxygen and the nitrogen of the air. The entire demonstration can be performed in a half hour.

The instructor should perform this experiment several times before attempting to demonstrate it to the class. The size and intensity of the arc, slight variations in the concentration of the caustic solution, and differences in the rate of flow of the air will affect the time required for the color change. I have, however, consistently obtained the above results under the conditions that I describe.

The RATES *and* MECHANISMS *of* SOME INORGANIC REACTIONS

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The kinetics of a number of familiar inorganic reactions are considered on the basis of the available experimental evidence. Quantitative rate studies have been made which measure the time necessary for completion of a certain fraction of the reaction. From data of this type, together with the information obtained by varying the initial concentrations of the reactants, and adding foreign salts, it is possible to gain an insight into the mechanism of the reaction. It is shown that for a number of apparently simple reactions the usual equation represents merely the initial and final states, and that there exist actually one or more intermediate steps. Oxidation-reduction, hydrolytic and catalyzed reactions are discussed in relation to their applications in analytical chemistry.

✦ ✦ ✦ ✦ ✦ ✦

THE study of reaction rates has been a rather neglected feature of the traditional courses in general and analytical chemistry. The reasons for this situation are perhaps not difficult to find: an already overcrowded course of study, and the fact that a satisfactory interpretation of reaction rates usually leads directly into physico-chemical considerations for which the student is not yet prepared.

Like other branches of science, kinetics has its own set of terms. Most of those used in this article are self-evident, but it is suggested that if the reader is not familiar with such concepts as reaction order, time of half-reaction, etc., he consult one of the excellent elementary presentations now available (*1*).*

The number of experimental investigations on the rates of inorganic and organic reactions is very large indeed. We may regard the data from two viewpoints. In the first place, the rate at which a given reaction proceeds may be of considerable practical importance. In industrial synthetic processes the object is to secure the highest yields in the shortest possible time, and the factors which influence the speed of the reaction are therefore important for the attainment of the desired ends.

The second viewpoint is concerned with the mechanism of the reaction. Theoretical advances are made from a knowledge of not only what enters into and results from a given reaction, but also from information as to what actually occurs during the reaction. It has been demonstrated repeatedly that the probability of more than two bodies reacting by collision is very small. If, therefore, the stoichiometrical equation of a reaction would necessitate ten molecules reacting to give the products, we are quite certain that the actual process must be something quite different from a ten-body collision. It is found as a matter of experiment that a great many reactions do proceed by means of several steps, each of which is usually bimolecular (or more rarely monomolecular or trimolecular).

In these cases the stoichiometric reaction is nothing more than the overall reaction—the sum of several kinetic steps. It is the purpose of this article to indicate how rate studies have helped to establish this for a number of familiar reactions.

For example, it has long been known that in the organic system acetone plus bromine

$$CH_3COCH_3 + Br_2 \longrightarrow CH_3COCH_2Br + Br^- + H^+$$

the rate of reaction is not directly proportional to the acetone and bromine concentrations as might be inferred from the above equation, but it depends on the acetone concentration and on the hydrogen-ion concentration, and is quite independent of the bromine concentration. More recently, King has shown that the rate of the reaction

$$S_2O_8^- + 2S_2O_3^- \longrightarrow 2SO_4^- + S_4O_6^-$$

depends directly on the persulfate concentration and is almost independent of the thiosulfate concentration (instead of varying as the *square* of the latter). Hydrogen ion also accelerates this reaction (*2*).

As another example, the familiar reaction

$$2Fe^{+++} + Sn^{++} \longrightarrow 2Fe^{++} + Sn^{++++}$$

is not third order as it was first thought to be, but under proper experimental conditions it can be shown to be of the second order. This will be considered later in more detail.

Two general methods of attack are used in kinetic investigations. The first, as already indicated, is to vary the concentrations of reactants entering the overall equation one at a time (and the hydrogen ion always present in aqueous solution) and to study the effect upon the observed rate. The second is to study the effect of various neutral salts upon the rate. In short, according to the theory developed chiefly by Brønsted, the rates of ionic reactions will be influenced by salts in a manner which depends primarily upon the ionic charge of the reactants. Thus if the ions (or neutral molecules) A and B react to form a complex

* Number references refer to the Literature Citation at the end of this article, letters to reactions summarized in Table 3.

X, which then decomposes to give the products, the rate is given by the expression $r = k_0 C_A C_B \left(\frac{f_A f_B}{f_X}\right)$ where k_0 is a constant independent of concentration, C_A and C_B are the concentrations of the molecules A and B, and the f's are the activity coefficients, respectively, of A, B, and X. The factor within the brackets (known as the kinetic activity factor, F) summarizes the effect of salts upon the rate, since it includes the variation of each constituent activity coefficient with the salt concentration. The latter is usually expressed in terms of *ionic strength* μ. Table 1 gives a summary (*3*).

TABLE 1

SALT EFFECTS AS A FUNCTION OF THE ELECTRIC CHARGE TYPE

Example	Type	Kinetic Activity Factor	Predicted Salt Effect at 0.1 M	Concentration Dependence
I.	$A^+ + B^0 \rightleftarrows X^+$	$\frac{f_A f_0}{f_1}$	0.96–1.04	Linearly Positive or Negative
II.	$A^+ + B^+ \rightleftarrows X^{++}$	$\frac{f_A f_1}{f_2}$	1.22	Exponentially Positive
III.	$A^+ + B^- \rightleftarrows X^0$	$\frac{f_A f_1}{f_0}$	0.49	Exponentially Negative
IV.	$A^{++} + B^- \rightleftarrows X^+$	$\frac{f_A f_1}{f_1}$	0.40	Exponentially Negative
V.	$A^{++} + B^+ \rightleftarrows X^{+++}$	$\frac{f_A f_1}{f_3}$	2.80	Exponentially Positive

The charge of X is equal to that of the sum of A and B. For a reaction between a singly charged ion and a neutral molecule (Example I) the effects of numerator and denominator cancel to a first approximation. Therefore, the variation of F with μ will be due solely to the effect upon the activity coefficient of the neutral molecule. This, while slight, may be either linearly positive or negative. On the other hand, when both A and B are charged, the variation of F with μ may be considerable and depends exponentially on the ionic strength.

The power of this kinetic method lies in the fact that it is possible to tell something about the charges of the ions involved in the reaction from the experimentally determined salt effect. Graphical plots of the relations between ionic strength and the rates of numerous reactions are given elsewhere (*3*, *1b*).

An Orienting Hypothesis.—An interesting preliminary note on the nature of slow oxidation-reduction reactions has recently been published by Shaffer (*4*). He states that in unsymmetrical cases, where the number of electrons lost by the reductant is not the same as the number required by the oxidant, the reaction is likely to be slow. For example, the reactions $Ce^{+++} \rightleftarrows Ce^{++++} + e$ and $Tl^+ \rightleftarrows Tl^{+++} + 2e$ are each known to be rapid in N sulfuric acid at room temperature with suitable reductants or oxidants. However, the reaction

$$2Ce^{++++} + Tl^+ \longrightarrow 2Ce^{+++} + Tl^{+++}$$

is exceedingly slow, so that the period of half reaction is a thousand hours or greater. Even raising the temperature to the boiling point does not produce rapid reaction. Catalysts such as manganous salts and platinum black will, nevertheless, considerably accelerate the rate.

Although this is the only case presented by Shaffer, from the material given below it can be seen that the rule holds very well. No examples of slow reactions in "symmetrical" cases come to mind, except where oxygen is involved. This means that there must result either less probable tri-molecular collisions, or else the reaction must proceed through several steps. These may all be bi-molecular, but they need not be. Nevertheless, it seems to be an experimental fact that the reaction will be slow, although exceptions do occur (for example, the familiar rapid reaction

$$2S_2O_3^= + I_2 \longrightarrow S_4O_6^= + 2I^-)$$

PERMANGANATE-CHROMIC REACTION

Investigation has shown that the reduction of permanganate ion proceeds by a complicated mechanism. In a recent paper on the reaction with oxalate ion some eight intermediate steps are considered (*5*). The reaction with chromic ion

$$3MnO_4^- + 5Cr^{+++} + 8H_2O \longrightarrow 3Mn^{++} + 5CrO_4^= + 16H^+$$

exhibits many interesting features. The following, taken from the work of Fales and Roller, will serve as illustration (*6a*).

At the start the reaction mixture contained MnO_4^- 0.00144 M, Cr^{+++} 0.0227 M, H_2SO_4 2.92 M, kept in a thermostat at 25.1°C. At various time intervals 25 cc. of the reaction mixture was pipetted out and poured into a solution containing excess potassium bromide

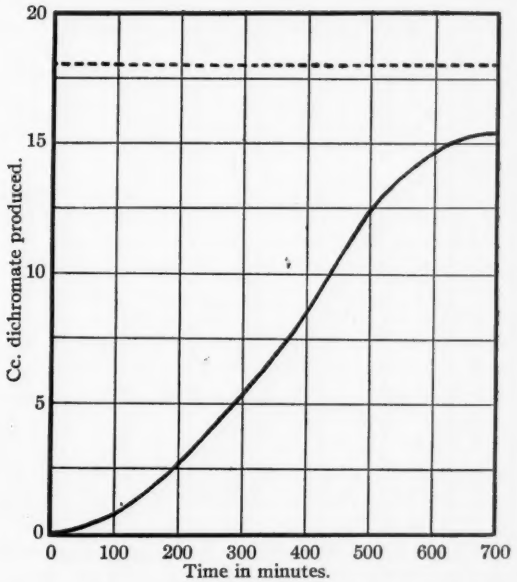


FIGURE 1.—REDUCTION OF MnO_4^- BY Cr^{+++} IN SULFURIC ACID

and sulfuric acid. The permanganate, unreduced by the chromic ion, reacted instantly with the potassium

bromide, and the bromine formed was extracted with carbon disulfide. The dichromate remaining was then titrated electrometrically with 0.01 *N* ferrous sulfate. In the absence of sunlight there is no reduction of dichromate by the potassium bromide. The results are plotted in Figure 1. As can be seen, there is a moderate initial rise, followed by a steeper one, and then a gradual tapering off as time passes. The dotted line gives the stoichiometrical equivalent, showing that the reaction is not complete even after seven hundred minutes.

Three experiments were next made to determine the order of the initial reaction (Table 2).

TABLE 2

ORDER OF THE INITIAL REACTION

Relative MnO_4^- Conc.	1	2	1
Relative Cr^{+++} Conc.	1	1	0.5
Cc. $Cr_2O_7^=$ Produced	*Minutes*	*Minutes*	*Minutes*
0.1	23	11	40
0.2	36	18	70

In the first column is given the amount of dichromate produced, in the second, third, and fourth the time required to produce this amount of oxidation. It is thus evident that thirty-six minutes are required to produce 0.2 cc. of dichromate when the MnO_4^-/Cr^{+++} ratio is unity, and only eighteen minutes when the permanganate concentration is doubled. Halving the chromic concentration increases the time to seventy minutes. For a second order reaction the time required for a given percentage of oxidation is inversely proportional to the concentration of each reactant, and it is seen that this relationship is sustained here within the experimental error. Thus, rate $= -d(MnO_4^-)/dt = k(MnO_4^-)(Cr^{+++})$, corresponding to the reaction

$$MnO_4^- + Cr^{+++} \longrightarrow Mn^{++++} + CrO_4^=$$

Halving the sulfuric acid concentration has practically no effect; therefore, hydrogen ion does not enter the rate step.

It must be remembered that the above description holds only for the initial stage of the reaction; further complications arise as the reaction proceeds. Also, although the potential of the system MnO_4^-/Mn^{++} varies markedly with the hydrogen-ion concentration, and with it the *ability* of permanganate to react with a given reductant, the experimental fact in this case is that the *rate* of a possible reaction is not affected. [For systems in which the rate is a function of the oxidation-reduction potential see (*7a*).] The treatment given here does not affect the writing and balancing of oxidation-reduction equations in terms of the overall reaction, since these can be satisfactorily developed without considering the intermediate mechanism (*7b*).

The increase in rate during the second stage of the reaction (Figure 1) is due to autocatalysis by the products of the reaction. This can be indicated only in outline. For example, the action of MnO_4^- upon Cr^{+++} to give Mn^{++++} is slow. A further reaction between Mn^{++++} and Cr^{+++} is much faster. However, the removal of Mn^{++++} through the reaction

$$Mn^{++++} + Mn^{++} \longrightarrow 2Mn^{+++}$$

is about 5.61 times faster than the second reaction. In addition, trivalent manganese readily forms complexes and the dissociation

$$Mn(HSO_4)_3 \longrightarrow Mn^{+++} + 3HSO_4^-$$

is slow.

From the above the experimenters found that the intermediate stage could be represented by the overall equation

$$Cr^{+++} + Mn^{+++} + Mn^{++++} + 4H_2O \longrightarrow CrO_4^= + 2Mn^{++} + 8H^+,$$

oxidation by Mn^{+++} taking place only in conjunction with the quadrivalent form.

The rate in the final stage (Figure 1) is affected by the increasing formation of the end product Mn^{++}, which retards the oxidation. For estimates of the concentrations of the intermediate manganese ions at various stages, reaction constants, etc., the original paper should be consulted.

The reduction of permanganate has also been studied in alkaline solution:

$$4MnO_4^- + 4OH^- \longrightarrow 4MnO_4^= + 2H_2O + O_2$$

The reaction is quite slow (it was followed up to three hundred twenty hours) and seems to be second order with respect to the permanganate concentration. The rate is also a function of the alkali concentration (*6b*).

BIVALENT SILVER REACTIONS

A. A. Noyes and his co-workers have shown in a very interesting series of papers (*8*) that when ozone is passed into a solution of silver nitrate in nitric acid there occurs a darkening, due to the formation of bivalent silver:

$$2Ag^+ + 2H^+ + O_3 \rightleftharpoons 2Ag^{++} + H_2O + O_2$$

This continues until a moderate proportion of the silver has been oxidized, depending on the concentration of silver, acid, ozone, and the temperature. A steady state is reached, however, which is due not to the reverse reaction, but to the decomposition of Ag^{++} by water. From a consideration of the factors which influence the rate, coupled with evidence that, though tripositive silver is produced, the bipositive state is the final result, the authors conclude that the mechanism is

$$Ag^+ + O_3 \longrightarrow AgO^+ + O_2 \text{ (slow)}$$
$$AgO^+ + Ag^+ + 2H^+ \rightleftharpoons 2Ag^{++} + H_2O \text{ (rapid equil.)}*$$

It was found, as might be expected from Example I, Table 1, that the salt effect is quite small.

The decomposition by water follows the relation

$$\text{rate} = -d(Ag^{++})/dt = k_1(AgO)^+ = k_2\frac{(Ag^{++})^2(H_2O)}{(Ag^+)(H^+)^2}$$

* The use of the terms rapid or rapid equilibrium throughout this paper does not necessarily imply that the reaction proceeds instantaneously, but merely that it proceeds so much faster than the slowest or rate step that it is without effect on the observed rate.

corresponding to the states

$$2Ag^{++} + H_2O \rightleftharpoons AgO^+ + Ag^+ + 2H^+ \text{ (rapid equil.)}$$
$$AgO^+ + H_2O \longrightarrow Ag^+ + H_2O_2 \text{ (slow)}$$
$$2Ag^{++} + H_2O_2 \longrightarrow 2Ag^+ + 2H^+ + O_2 \text{ (rapid)}$$

The rates of formation at 0.5° were followed up to about an hour, the rate of decomposition by water up to seven hours at 24°C., and twenty-three hours at 0.5°C.

REACTIONS INVOLVING IRON

The reaction

$$2Fe^{+++} + Sn^{++} \longrightarrow 2Fe^{++} + Sn^{++++}$$

has been mentioned previously. Early experimental work showed that ferric ion had a greater influence on the rate of reaction than had stannous ion when no foreign salts were added. Third order constants

$$\text{rate} = k(Fe^{+++})^2(Sn^{++})$$

could thus be obtained, although the value of K did depend on the initial concentration of reactants. Recent investigators have shown that this may be interpreted in terms of the salt effect theory outlined above. Trivalent ions produce greater effects on the activity coefficients of other ions than do divalent ions. The method adopted in this case—a general procedure first proposed by Brønsted for reducing salt effects to a minimum—was to study the reactions not in pure water but in concentrated salt solutions. Since the ionic strength was now quite large, the addition of a small amount of either reactant did not appreciably change the electrical environment. As a result, it was found that the rate of this reaction is proportional to the first power of the concentrations of both ferric and stannous ions. The absolute rate of reaction in salt solutions is of course different from that in water, but this is without influence on the question of the order of the reaction (*9*).

The oxidation of ferrous sulfate solutions by oxygen has been investigated by Lamb and Elder, who concluded that the rate was given by the expression

$$r = k(Fe^{++})^2(O_2)$$

Hydrogen ion up to 0.1 molar increased the rate, which then remained constant at higher acidities. General salt effects are absent for this reaction, but certain salts, such as those of copper exhibit marked catalytic effects (*10*).

The reaction

$$2Fe^{+++} + 2I^- \longrightarrow 2Fe^{++} + I_2$$

has received much attention. The rate expressions given are quite complicated. In concentrated salt solutions the reaction seems to be first order with respect to ferric ion, and second with respect to iodide ion. At higher salt concentrations the order of the latter comes nearer one. There are probably several reactions occurring at once (*11*). (See also *b, c, d, f.*)

PEROXIDE AND HALOGEN REACTIONS

The number and complexity of the reactions under this heading would require all of the space of this review for even a bare outline. Hydrogen peroxide is reduced in solutions containing hydriodic acid according to the equation

$$H_2O_2 + 2H^+ + 2I^- \longrightarrow I_2 + 2H_2O$$

On the other hand, if iodine solutions are used, there results oxidation of the hydrogen peroxide

$$H_2O_2 + I_2 \longrightarrow 2H^+ + 2I^- + O_2$$

From the above it follows that a steady state must be reached, with a constant concentration of H^+, I^-, and I_2, and that the only observable change with time will be decomposition of the peroxide

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

The bromine-bromide, chlorine-chloride, dichromate-chromic couples also catalyze the decomposition (*12*).

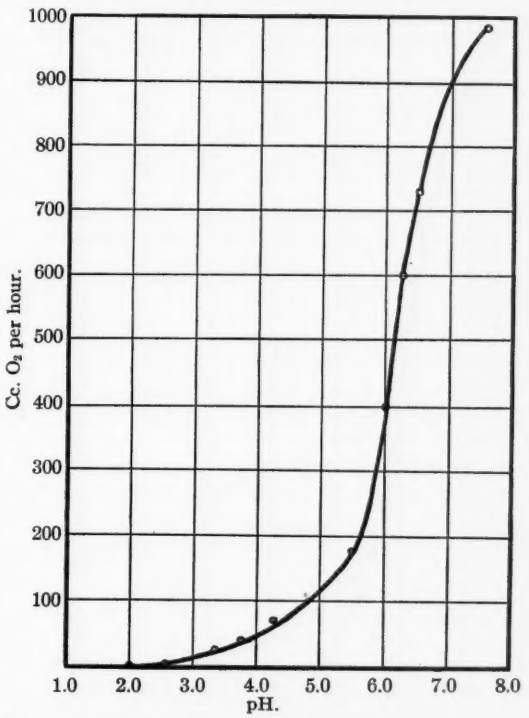


FIGURE 2.—EFFECT OF ACIDITY UPON RATE OF DECOMPOSITION OF 2200 CC. 30% HYDROGEN PEROXIDE

The rate of the reduction by I^- is governed by two simultaneous reactions, each of which enter as rate-determining steps

$$H_2O_2 + I^- \xrightarrow{k_1} H_2O + IO^-$$
$$H_2O_2 + H^+ + I^- \xrightarrow{k_2} H_2O + HIO$$

From this may be developed the equation

$$\text{rate} = -d(H_2O_2)/dt = k_1(H_2O_2)(I^-) + k_2(H_2O_2)(H^+)(I^-)$$

TABLE 3

	Stoichiometrical Reaction	Order	Rate Step or Equation	Temp. C.	Notes	Ref.
(a)	$S_2O_8^{=} + 2I^- \longrightarrow 2SO_4^{=} + I_2$	2	$r = k(S_2O_8^{=})(I^-)$	25°	positive salt effect	(58)
(b)	$S_2O_8^{=} + 2Fe^{++} \longrightarrow 2SO_4^{=} + 2Fe^{+++}$	2	$r = k(Fe^{++})(S_2O_8^{=})$	15.5°	negative salt effect	(59)
(c)	$S_2O_8^{=} + 2[Fe(CN)_6]^{\equiv} \longrightarrow 2SO_4^{=} + 2[Fe(CN)_6]^{=}$	2	$r = k(S_2O_8^{=})[Fe(CN)_6]^{\equiv}$	15°	in conc. salt solutions	(60)
(d)	$2[Fe(CN)_6]^{=} + 2I^- \longrightarrow 2[Fe(CN)_6]^{\equiv} + I_2$	3	$r = k[Fe(CN)_6]^{=}(I^-)^2$	25°	in conc. salt solutions	(61)
(e)	$NH_4^+ + CNO^- \longrightarrow NH_4CNO$	2	$r = k(NH_4^+)(CNO^-)$	70°	negative salt effect	(62)
(f)	$2[Fe(CN)_6]^{\equiv} + I_2 \longrightarrow 2[Fe(CN)_6]^{=} + 2I^-$	2	$r = k[Fe(CN)_6]^{\equiv}(I_2)$	14°	in 0.1 *N* KCl 0.02 *N* H_2SO_4	(59)
(g)	$2HBrO + BrO^- \longrightarrow BrO_3^- + 2H^+ + Br^-$	3 4	$-d(HBrO)/dt = k_2(HBrO)^2(BrO^-) = \frac{k_1(HBrO)^2(OH^-)}{}$	25°	in pH range 6.4–7.8	(63)
(h)	$BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$	4	$-d(BrO_3)/dt = k_4(BrO_3^-)(Br^-)(H^+)^2$	25°	salt effects indicate possible 5th order	(64)
(i)	$SCN^- + 4I_2 + 4H_2O \longrightarrow SO_4^{=} + 7I^- + 8H^+ + ICN^-$	2	$r = k(SCN^-)(IO^-)$	20°	in $NaHCO_3$ but not in NaOH solutions	(65)
(j)	$[Cr(H_2O)_4Cl_2]Cl + H_2O \longrightarrow [Cr(H_2O)_5Cl]Cl_2$ $[Cr(H_2O)_5Cl]Cl_2 + H_2O \longrightarrow [Cr(H_2O)_6]Cl_3$	1 1	$r = k_1[Cr(H_2O)_4Cl_2]^+$ $r = k_2[Cr(H_2O)_5Cl]^{++}$	25° 25°	k_1, k_2 functions of pH	(67)
(k)	$Na_4P_2O_7 + H_2O \longrightarrow 2Na_2HPO_4$	2	$r = k(H^+)(H_2P_2O_7^-)$	20–40°	in HCl + KCl	(66)
(l)	$2N_2O_5 \longrightarrow 2N_2O_4 + O_2$	1	$r = k(N_2O_5)$ $N_2O_5 \longrightarrow N_2O_3 + O_2$ (slow) $N_2O_5 \longrightarrow NO + NO_2$ (fast) $NO + N_2O_5 \longrightarrow 3NO_2$ (fast)	20°	in gas phase	(68)
(m)	$2HI \longrightarrow H_2 + I_2$	2	$r = k(HI)^2$	0°	in gas phase	(69)
(n)	$H_2 + Br_2 \longrightarrow 2HBr$		$\frac{d[2HBr]}{dt} = \frac{k_1[H^+]\sqrt{(Br_2)}}{k + \frac{2(HBr)}{(Br_2)}}$ $Br_2 \longrightarrow 2Br$ $Br + H_2 \longrightarrow HBr + H$ $H + Br_2 \longrightarrow HBr + Br$ $H + HBr \longrightarrow H_2 + Br$	200 to 300°	in gas phase	(70)
(o)	NH_4(amalgam) $\longrightarrow NH_3 + \frac{1}{2}H_2$	2	$2NH_4^+ + 2e \longrightarrow 2NH_3 + H_2$	0–20°	in metallic mercury	(71)

The bromide and chloride equations are similar.

On the other hand the oxidation involves the steps

$$I_2 + H_2O \rightleftharpoons H^+ + I^- + HIO \quad \text{(rapid equil.)}$$
$$HIO \rightleftharpoons H^+ + IO^- \quad \text{(rapid equil.)}$$
$$H_2O_2 + IO^- \xrightarrow{k_3} I^- + H_2O + O_2 \quad \text{(rate step)}$$

Since the equilibrium constants for the two rapid reactions have been determined, the concentration of IO^- can be solved for in terms of H^+, I^-, and I_2, giving the rate equation

$$r = -d(H_2O_2)/dt = k_3' \frac{(H_2O_2)(I_2)}{(H^+)^2(I^-)}$$

k_3' thus involves a reaction rate constant k_3, the hydrolysis constant of iodine, and the dissociation constant of HIO (*13*).

The equation for the bromine reduction is similar but involves hydrogen ion only to the first power, since

$$Br_2 + H_2O \rightleftharpoons HBrO + H^+ + Br^- \quad \text{(rapid equil.)}$$
$$HBrO + H_2O_2 \longrightarrow H^+ + Br^- + O_2 \quad \text{(rate step)}$$

Hydrogen peroxide studies of another sort have been made by Rudel and Haring (*14*). They measured the amount of oxygen given off from 2.2 liters of 30 per cent. hydrogen peroxide at 32°C. with and without the presence of various metallic salts. Figure 2 shows the amount of oxygen evolved per hour as a function of pH. These results are of interest since peroxide of this strength (Superoxol) has become a common reagent and a knowledge of its stability is therefore important.

Other halogen reactions are given in Table 3 (*a*, *d*, *f*, *g*, *h*, *i*). The mechanism of chlorate, bromate, and iodate formations and decompositions has been discussed in a comprehensive manner by Skrabal (*15*). These reactions have been shown to proceed through a number of intermediate steps, and it seems probable that in the apparently high-order reactions these are really monomolecular or bimolecular.

REACTIONS OF NITROUS AND NITRIC ACIDS

The decomposition of nitrous acid, investigated by Abel, Schmid, and their co-workers, affords a fine example of a complete kinetic study (*12*). In aqueous solution at 25°C. the reaction is

$$3HNO_2 \rightleftharpoons H^+ + NO_3^- + 2NO + H_2O$$

which proceeds initially by means of the steps

I. $4HNO_2 \rightleftharpoons N_2O_4 + 2NO + 2H_2O$ (rapid equil.)
II. $N_2O_4 + H_2O \longrightarrow HNO_2 + H^+ + NO_3^-$ (rate step)

which lead to the kinetic equation

III. rate $= -d(HNO_2)/dt = k(HNO_2)^4/(p_{NO})^2$

There is also evidence that step I merely represents the sum of several intermediates.

The reverse reaction for I and II is autocatalytic, but in the presence of nitrous acid the mechanism is

IV. $HNO_2 + H^+ + NO_3^- \longrightarrow N_2O_4 + H_2O$ (rate step)
V. $N_2O_4 + 2NO + 2H_2O \longrightarrow 4HNO_2$ (fast)

so that the kinetic equation for the *production* of nitrous acid becomes

VI. $d(HNO_2)/dt = k(HNO_2)(H^+)(NO_3^-)$

At equilibrium, the velocity of decomposition is equal to the rate of the forward reaction (III) minus the rate of the reverse one (VI).

The kinetics of the oxidation of arsenious acid by nitric acid have been investigated by the same workers (*16*).

$$3H_3AsO_3 + 2HNO_3 \longrightarrow 3H_3AsO_4 + 2NO + H_2O$$

It is known from kinetic and other experiments that nitric acid which has been carefully freed from the oxides of nitrogen lacks the oxidizing properties of the usual reagent nitric acid. For the above reaction the mechanism which has been proposed includes, first, the production of nitrous acid from nitric acid (starting

with a small initial concentration of the former)

I. $HNO_3 + HNO_2 \longrightarrow N_2O_4 + H_2O$ (fast)
II. $N_2O_4 + 2NO + 2H_2O \longrightarrow 4HNO_2$ (fast)

followed by the rapid reaction

III. $2HNO_2 \longrightarrow N_2O_3 + H_2O$

and the rate step

IV. $N_2O_3 + H_3AsO_3 \longrightarrow H_3AsO_4 + 2NO$

which is expressed by the rate equation

$$r = k(H_3AsO_3)(HNO_2)^2$$

REACTIONS OF COMPLEX IONS

The formation and decomposition of many complex ions proceed at measurable rates. Rearrangements of linkages, such as those involved in oxidation-reduction reactions requiring the transfer of oxygen, many ferro-ferricyanide reactions, and the formation of urea from ammonium and cyanate ions (*e*) are usually slow processes. The reactions between cobalt and cyanide ions or silver ion and ammonia go too fast for present experimental technic (*17a*).

Kinetic studies of the polythionic acids have shown that the reaction

$$S_5O_6^{=} + 2SO_3^{=} \longrightarrow S_3O_6^{=} + 2S_2O_3^{=}$$

occurs in two bimolecular stages:

$$S_5O_6^{=} + SO_3^{=} \longrightarrow S_4O_6^{=} + S_2O_3^{=}$$
$$S_4O_6^{=} + SO_3^{=} \longrightarrow S_3O_6^{=} + S_2O_3^{=}$$

The first reaction is about twenty times faster than the second (*18a*). Rate studies have been made of several other polythionic reactions (*18b*).

Many examples can be found among the so-called Werner complexes. In most cases the substitution of one radical for another in the "inner sphere" is slow. Thus, brompentamminecobaltic ion reacts slowly with aqueous alkali

$$[Co(NH_3)_5Br]^{++} + OH^- \longrightarrow [Co(NH_3)_5OH]^{++} + Br^-$$

The reaction exhibits a negative salt effect. If, however, mercuric ion is added instead of alkali the substitution

$$2[Co(NH_3)_5Br]^{++} + Hg^{++} + 2H_2O \longrightarrow 2[Co(NH_3)_5H_2O]^{+++} + HgBr_2$$

occurs. The reaction is nevertheless bimolecular, following the kinetic equation

$$\text{rate} = k[Co(NH_3)_5Br]^{++}[Hg^{++}]$$

and has a positive salt effect (*19a*).

The cations of many ammines such as $[Ir(NH_3)_5Cl]^{++}$, $[Cr(NH_3)_5Br]^{++}$, and $[Co(NH_3)_5NO_3]^{++}$ also interchange in neutral solution, and less rapidly in acid solution (*19b*). Other reactions are subject to hydrogen-ion catalysis. Pedersen found the rate of the decomposition

$$[Co(NH_3)_4CO_3]^+ + 2H^+ + 2H_2O \longrightarrow [Co(NH_3)_4(H_2O)_2]^{+++} + CO_2$$

to depend on two factors, one dependent on the hydrogen-ion concentration, the other independent of it, and the rate expression may, therefore, be considered as the sum of two second order constants (*20*).

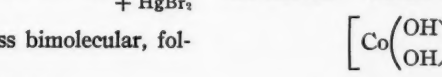
Nitrito salts such as $[Co(NH_3)_5(ONO)]Cl_2$ are slowly transformed in the solid state, and very rapidly in solution, to the more stable nitro compounds. Various forms of the latter also occur. According to Brønsted the *trans*$[Co(NH_3)_4(NO_2)_2]NO_3$ exists in two allotropic forms. In the solid state the α form (yellow needles) is very slowly converted to the stable β form (brown powder), the time of transformation being estimated as of the order of twenty-five years. In aqueous solution at 0° the change can be noticed in a few hours, at 25° in ten minutes (*21*).

Many interesting transformations take place among stereoisomeric forms. Thus repeated evaporation of a solution of the green *trans*[Co en_2Cl_2]Cl—en is a symbol for ethylenediamine—yields the violet *cis* form. On the other hand, with a solution containing up to 12.5 per cent. HCl the solid phase in equilibrium with the solution slowly changes over to the composition *cis*[Co en_2Cl_2]Cl·H_2O. If stronger acid is used there results merely an acid form of the *trans* compound [Co en_2Cl_2]Cl·HCl·H_2O (*22*).

Heating an alkaline solution for a half hour leads to the reaction *trans*[Co en_2Cl_2]Cl → *cis*[Co $en_2(H_2O)Cl$]-Cl_2 → *cis*[Co $en_2(H_2O)_2$]Cl_3 (*23a*). When a solution of the carbonatotetrammine salt is acidified with HCl the violet *cis*$[Co(NH_3)_4Cl_2]Cl$ results, which is more or less rapidly converted to the green *trans* form, depending on the temperature.

Some decompositions are photochemical. Investigation of the first order reaction $[Co(NH_3)_4(NO_2)_2]Cl + 3H_2O \rightarrow Co(OH)_3 + 2\ NH_4NO_2 + NH_3 + NH_4Cl$ in dilute aqueous solution indicates that the *trans* form is the more stable. After illumination of a 0.001 molar solution for an hour 55 per cent. of the *cis* form had decomposed, while only 48.8 per cent. of the *trans* form was destroyed. Other cases are also known (*23b*).

Many complexes can be resolved into optically active forms which, however, racemize fairly rapidly in solution. Thus a 0.25 per cent. solution of the *d* or *l* *cis*-[Co $en_2ClBr]NO_3$ is inactive after forty-five minutes (*23c*). Active complexes entirely free of carbon are also known. Werner found that



racemized quite rapidly in aqueous solution but less rapidly in the acetone-water mixtures in which the specific rotation was determined (*24*).

WATER REACTIONS

Numerous studies on slow hydrolyses are recorded in the literature (*25*). Among these may be mentioned the early work of Goodwin on ferric chloride, and of Bjerrum on chromic chloride (*j*). A recent study has been made on the hydrolysis of titanium sulfate solutions at the boiling point, under conditions which prevail in the industrial preparation of titanium pigments (*26*).

The entire subject has been of interest to colloid chemists because the properties of many colloidal solutions are a function of time. Certain substances when freshly precipitated are readily soluble in appropriate solvents, but after they have stood they become insoluble. This "aging" is often marked by color changes. It is interesting to note that a similar process has been observed in the ammonia system of compounds. If copper nitrate dissolved in liquid ammonia is treated with a base such as KNH_2 a precipitate is formed which changes color on standing (*27a*).

The mechanism of the changes which take place in hydrous alumina sols has been pictured as follows:

$$[Al(H_2O)_6]^{+++} \rightleftharpoons H^+ + [Al(H_2O)_5OH]^{++} \quad \text{(fast, aided by heat and alkali)}$$

$$2[Al(H_2O)_5OH]^{++} \rightleftharpoons \left[(H_2O)_4Al\begin{matrix}OH\\OH\end{matrix}Al(H_2O)_4\right]^{++++} + 2H_2O \quad \text{(slow)}$$

The product of the second step may react still further by dissociation of a hydrogen ion from the water molecules contained therein, until very large ions of colloidal dimensions form. These changes are quite slow; the pH of alumina sols has been shown to be still changing some two months after preparation. Since the reverse reactions are also slow it would not be expected that the aged sols would be readily soluble in dilute acids. For a detailed consideration of systems of this type see (*28*).

The reaction of many acid anhydrides with water is slow. It has been observed that in acidimetric titrations with phenolphthalein as the indicator the color slowly faded after the end-point was reached. This is not due to absorption of carbon dioxide from the air, but to slow reaction of the carbon dioxide already present in solution. Investigation has shown that there are two simultaneous reactions

$$CO_2 + H_2O \longrightarrow H_2CO_3$$
$$CO_2 + OH^- \longrightarrow HCO_3^-$$

the constant for the first reaction is 7×10^{-3}, for the second 3.7×10^3, at 13.7°C. Carbonic acid is a considerably stronger acid than one might suppose. The familiar constant

$$K = \frac{(H^+)(HCO_3^-)}{(H_2CO_3 + CO_2)} = 3.1 \times 10^{-7} \text{ at } 18°$$

includes the sum of hydrated and unhydrated carbon dioxide. The true dissociation constant is

$$K = \frac{(H^+)(HCO_3^-)}{(H_2CO_3)} = 3.1 \times 10^{-4} \text{ at } 13.7°$$

The rate of the first order decomposition

$$H_2CO_3 \longrightarrow CO_2 + H_2O$$

has also been measured and gives a constant of 8 at 13.5° (*17b*).

Reaction such as

$$6ClO_2 + 3H_2O \longrightarrow 5HClO_3 + HCl$$

and

$$2ClO_2 + 2KOH \longrightarrow KClO_2 + KClO_3 + H_2O$$

are also slow (*29a*).

The rate of reaction of dry metallic nitrides with water may vary considerably. Mg_3N_2 and Zn_3N_2 hydrolyze very rapidly; Mn_3N_2 and W_2N_3 do so only very slowly. Chromic and iridium sulfides prepared in the dry state and heated strongly are not readily attacked by water afterward (*29b*).

ACID CATALYZED REACTIONS

The rates of a large number of reactions are markedly affected by the acidity of the solvent used. Several reactions which have been studied at rather low acidities are given in Table 4. They involve the sodium or ammonium salts of monometaphosphoric or pyrophosphoric acids. The third column gives the initial concentration of the salt used, in moles per liter, the fourth the molarity of the solvent. The time for fifty per cent. or ninety-five per cent. hydration has been interpolated from the original data where necessary.

TABLE 4
RATES OF HYDRATION OF SALTS

Reaction	Temp. °C.	Conc. Salt	Conc. HCl	Time for Given Degree of Hydration 50%	95%	
$NaPO_3 + H_2O \rightarrow NaH_2PO_4$	45	0.500	0.339	11 hr.	220 hr.	
		0.300	0.339	4.6	100	(*30*)
	55	0.100	0.100	5.6	117	
$NH_4PO_3 + H_2O \rightarrow NH_4H_2PO_4$	55	0.100	0.100	5.2	86	(*31*)
$Na_4P_2O_7 + H_2O \rightarrow 2Na_2HPO_4$	45	0.225	0.350	850	4035	(*32a*)
		0.225	0.500	357	1553	

The reaction

$$3NaPO_3 + 2H_2O \longrightarrow Na_2H_2P_2O_7 + NaH_2PO_4$$

gives equimolecular quantities of both products in alkaline solution (*33*). Recently the temperature coefficient of the acid hydration of sodium pyrophosphate has been investigated over a range of temperatures and acid concentrations (*32b*). (See also *k*.)

Several reactions go on at very high acidities. Persulfuric acid decomposes in sulfuric acid in two consecutive steps:

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4$$
$$H_2SO_5 + H_2O \longrightarrow H_2O_2 + H_2SO_4$$

The rates of these reactions have been measured in from 10 *N* to 5 *N* sulfuric acid (*34*). The rates of reactions such as the decomposition of formic acid in sulfuric acid, and the hydrolysis of cyanamide in the same solvent can now be definitely correlated with a function of the acid concentration, even at very high acidities (*35*).

SOME APPLICATIONS OF SLOW REACTIONS

The fact that a reaction is slow may not necessarily be a drawback; on the contrary, the existence and usefulness of certain reagents and operations depend largely on time reactions. Transformations among allotropic modifications of the elements may also be slow: metastable forms of sulfur and phosphorus are only gradually converted to their more stable forms (*36*). The metastable equilibrium of white tin, which seems to be maintained continually, is an everyday example. The rate of transformation reaches a maximum as the temperature is lowered below the transition point (*37*).

The sensitivity to hydrogen ions of certain reactions, such as the decomposition of diazoacetic ester, has been used for many years for the determination of pH. Sandell and Kolthoff have recently proposed an analogous method for determining extremely small concentrations of iodide ion through its effect upon the reaction

$$As^{+++} + 2Ce^{++++} \longrightarrow As^{+++++} + 2Ce^{+++}$$

the rate of reaction being directly proportional to the iodide-ion concentration (*38*).

As another example, we may take the reaction between ceric sulfate and thiosulfate ion, which is negligibly slow under analytical conditions. If, however, the two fast reactions

$$2Ce^{++++} + 2\ I^- \longrightarrow 2Ce^{+++} + I_2$$
$$I_2 + 2S_2O_3^{=} \longrightarrow 2I^- + S_4O_6^{=}$$

are utilized, thiosulfate solutions can easily be standardized against ceric sulfate by adding a certain quantity of iodide ion to the latter (*39*).

The separation and detection of elements in mixtures often depend on slow reactions. Thus Thornton and Roseman have found it possible to titrate iron in the presence of titanium if the acid solution from the Jones reductor was aërated for ten to thirty minutes and then titrated. Under these conditions only the reaction $Ti^{+++} \rightarrow Ti^{++++}$ is rapid and complete, and since the titanic titanium does not interfere, the ferrous iron which remains can be readily determined by the usual methods. Aërating an acid solution of ferrous ammonium sulfate for twelve hours resulted in oxidation of only one part in seven thousand (0.014 per cent.) of the total ferrous iron (*40*).

The separation of calcium from magnesium as the oxalate depends in part on the slowness with which magnesium oxalate forms as compared with calcium oxalate (*41a*). Several studies have shown that the reaction was not complete after three hundred hours, and that a supersaturation of three hundred times the equilibrium concentration of magnesium oxalate could be obtained (*42*). In precipitating lead sulfate in the presence of bismuth, a basic bismuth sulfate can be obtained if the solution stands too long (*41b*).

The rate of precipitation of strontium sulfate from its supersaturated solutions has been followed by the change in conductivity. Equilibrium was not reached in some cases after six hundred hours. In this reaction there is apparently an intermediate colloidal stage after the reactants are mixed (*43*). Hill and his coworkers have found cases where solutions remained supersaturated in the presence of the solid phase during a period of at least three months (*44*).

Many sulfides precipitate slowly from aqueous solution. A 0.05 *M* zinc sulfate solution in 0.5 *N* sulfuric acid shows no precipitate for three-quarters of an hour when the solution is saturated with hydrogen sulfide. And similar saturation of a 0.063 *M* zinc sulfate solution in 2 *N* sulfuric acid results in precipitation of only a quarter of the zinc in two and a half months, and half precipitation in five months. The problem of sulfide precipitation has been reviewed recently (*45*).

The changes in certain colloidal hydroxides with time have been touched upon briefly above. Sulfides exhibit similar behavior. Black mercuric sulfide is slowly converted to the red modification on heating with alkali sulfides; flesh-colored manganous sulfide is transformed to a grey-green form. When freshly precipitated, zinc sulfide is readily soluble in dilute acids; the aged form is not. Although they will not precipitate by themselves from acid solution, nickel and cobalt sulfides once formed by a momentary excess of alkali will redissolve in the acid solution only very slowly. A study of the rate of solution of nickel sulfide in hydrochloric acid is summarized in Figure 3.

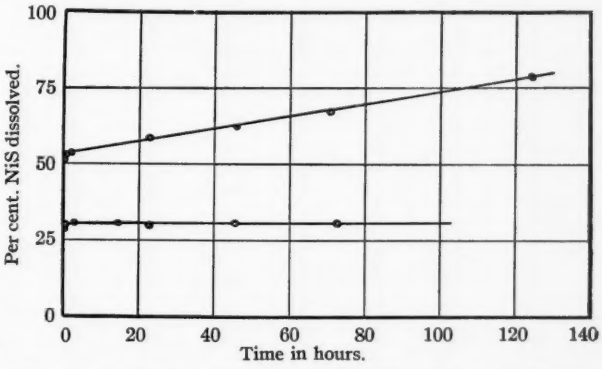


FIGURE 3.—RATE OF DISSOLUTION OF NiS. CURVE 1—WASHED SAMPLE IN 2 NORMAL HCl; CURVE 2—SAMPLE IN 2 NORMAL HCl SATURATED WITH H_2S

The effect of saturating the hydrochloric acid with hydrogen sulfide is given by the lower curve (*46*).

Many substances can be used as reagents if their decompositions are not too rapid. Thus, although there can be no large concentration of cobaltic ion in an aqueous solution, certain cobaltic compounds can exist in the presence of water if they are extremely insoluble (cobaltic hydroxide) or are in the form of slightly ionized complexes (cobaltammines). Nevertheless, there may be some slow reaction of the small concentration of cobaltic ion produced by ionization with the hydroxyl ion of the solvent or with any more easily oxidizable material present.

Other substances which have a great tendency to be oxidized may also react with the solvent. For example, solutions of chromous salts liberate hydrogen slowly, through reduction of hydrogen ion. Nevertheless, standard solutions of chromous sulfate in 0.03 *N* sulfuric acid may be kept for a month if oxygen is excluded (*47*). The divalent ions Sm^{++}, V^{++}, and W^{++} react more rapidly with water, especially if platinum black is introduced. Sodium dissolves quite rapidly in liquid ammonia, but the subsequent reaction with the solvent, which gives $NaNH_2$ and H_2, is exceedingly slow (*27b*).

Self oxidation-reduction reactions of the type

$$2HSnO_2^- \longrightarrow SnO_3^= + Sn + H_2O$$

may also be relatively slow, but the stannite solutions which find application in the detection of bismuth cannot be preserved very long (*41c*). Sometimes slow reactions may cause difficulties in analytical procedures. Thus, in the iodimetric determination of chromate an error is produced by the requirement of an excess of thiosulfate. This was formerly thought to be due to oxidation of iodide ion by the air. Hahn has demonstrated, however, that there is a chromic-thiosulfate complex formed when chromate is reduced in the presence of thiosulfate (although not by simple mixing of chromic ion with thiosulfate). The slow release of thiosulfate from the complex prevents accurate titration unless special precautions are taken (*48*).

A NOTE ON FAST REACTIONS

By the use of flow methods it has been possible to measure experimentally the rates of some very rapid reactions (see summary in *17a*). LaMer and Read have studied the neutralization of sodium dichromate by sodium hydroxide, concluding that the mechanism was

$$Cr_2O_7^= + H_2O \longrightarrow 2HCrO_4 \quad \text{(rate step)}$$
$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^= \quad \text{(fast)}$$
$$H^+ + OH^- \longrightarrow H_2O \quad \text{(fast)}$$

In dilute aqueous solution the concentration of water is great and constant, and therefore the first reaction appears as of the first order with respect to dichromate. The time of half reaction is given as 0.0785 second (*49*).

Francis has measured the relative rates of some fast reactions by employing a competitive method (*50*). It consisted essentially of adding to a mixture of substance A and substance B a third component C in amount insufficient to react completely with both. From the amounts of the products of the reaction of A with C, and B with C the relative rates of the reactions could be determined, on the assumption that the absolute rates were unaffected (or equally affected) by the presence of the other substances. That this may not always be true was shown above in the case of the persulfate-iodide reaction in the presence of thiosulfate.

It was found that if, for example, one millimole of $SnCl_2$, $NaHSO_3$, and Br_2 were mixed the latter reacted equally fast with both, since approximately one half of the $SnCl_2$ and the $NaHSO_3$ was left unchanged. Iodine also reacts equally fast with both reducing agents. Comparisons with the rates of organic reactions were also made, as in the competition of titanous chloride and *p*-toluidine for bromine. Table 5 gives the results, which are based relative to $TiCl_3$ as substance B, and Br_2 as the C standard.

TABLE 5

RELATIVE RATES OF REACTION

Component A	$Na_2S_2O_3$	HI	$NaHSO_3$	$SnCl_2$	$NaAsO_2$	$K_4Fe(CN)_6$
Relative Rate	15	14	8.6	4.1	4.0	2.4
Component A	$FeSO_4$	$FeCl_2$	$NaNO_2$			
Relative Rate	0.3	0.3	0.003			

Thus from the table it is found that with bromine $NaAsO_2$ reacts four times as fast as does $TiCl_3$. Francis also found that sodium thiosulfate reacts with iodine about 1.7 times as fast as does sodium bisulfite when the measurements were made in water, and about forty-three times as fast when they were made in eighty per cent. alcohol.

OTHER REACTION RATE STUDIES

In concluding, we mention briefly some other examples of reaction rate studies which may be of interest to the inorganic chemist. The subject of heterogeneous reaction rates has been comprehensively treated by Taylor (*51*). Of special interest are the rates of solution, including those of solids in water, metals in acids, and the subject of contact catalysis as exhibited in many important technical reactions. The kinetics of gas reactions have been extensively reviewed (*52*, *53*, *57*).

For comparison with the material reviewed in this paper several gas reactions have been included in Table 3. The decomposition of nitrogen pentoxide (*l*), which proceeds unimolecularly, has been studied in both the gas phase and in solution. The dissociation of hydrogen iodide is a familiar example of a bimolecular reaction (*m*); the combination of hydrogen and bromine is a more complicated halogen reaction (*n*). Finally the decomposition of ammonium amalgam (*o*) has been given as an example of a reaction taking place in a metallic solvent, mercury.

A beginning has been made in the study of certain important reactions, such as the rate of oxidation of graphite by steam, and the rate of reduction of carbon dioxide by graphite (*54*). Other studies of gaseous reactions have been made in connection with the development of anti-knock agents for motor fuels.

Many attempts have been made to provide a theoretical foundation for reaction rate experiments; a historical sketch is given by Eyring (*55*). This has been extended to heterogeneous reactions. Topley, for example, has recently made a calculation on the absolute rate of the thermal decomposition

$$CuSO_4 \cdot 5H_2O \longrightarrow CuSO_4 \cdot H_2O + 4H_2O$$

by starting with the model of the inorganic chemist $[Cu(H_2O)_4]^{++}[SO_4 \cdot H_2O]^=$ and applying statistical mechanics thereto (*56*).

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SPRING MEETING, DIVISION OF CHEMICAL EDUCATION

The next meeting of the Division of Chemical Education of the American Chemical Society, to be held at Chapel Hill, North Carolina, April 12th–15th, will feature an informal colloquium on the teaching of qualitative analysis. Any members of the Division who may wish to take part in this are invited to communicate with the Secretary of the Division, Brown University, Providence, Rhode Island.

N. W. RAKESTRAW, *Secretary*

SOME NEW EXPERIMENTS *on* SILICIC ACID GELS

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Several interesting and rather simple experiments covering some conditions in the formation and properties of silicic acid gels are described. The experiments have been devised from the results obtained in the author's laboratory over a period of six to eight years in a series of studies on silicic acid gels. The results of some of these investigations have been published. The experiments have been performed successfully by students in our laboratory and are described here so that they may be available for others.

✦ ✦ ✦ ✦ ✦ ✦

INTRODUCTION

IT HAS been known since the observations of Graham (*1*) that when a solution of sodium silicate and a solution of some acid are mixed, the resulting mixture may gradually become opalescent and set to a rather firm gel. This is one of the easiest gels to prepare and the control of conditions can be made very satisfactory, a feature almost entirely lacking in the preparation of many gels. As a result of the findings of many investigators it would appear that we are dealing here with one of the simplest of all the gels known. The properties are interesting and typical of gel structure.

The time of set of the gel mixture has been found to depend, among other factors, upon the concentration of silica in the mixture, upon the temperature, the hydrogen-ion concentration, the acid used, and the presence and concentration of various salts or foreign substances. The experiments to be described involve studies of the effect of temperature, hydrogen-ion concentration, presence and concentration of certain impurities, and effect of setting upon the electrical conductivity.

Certain simple solutions are required. It is not absolutely necessary to employ the concentrations recommended, but on the other hand we have found the concentrations recommended to work best in many experiments performed in our laboratory.

PREPARATION OF SOLUTIONS

Sodium Silicate.—Commercial water glass should be diluted with distilled water until a solution equivalent to 1.25 normal sodium hydroxide is obtained. We have had best results using the E brand silicate manufactured by the Philadelphia Quartz Company. If 100 cc. of this E brand silicate is diluted to 320 cc. with distilled water, approximately the right normality will be obtained. The normality, as its equivalent in sodium hydroxide, may be determined by titration with a standard sulfuric acid solution, using methyl orange as indicator. Best results will be secured here if the silicate is run into the acid, the latter having first been diluted with about an equal volume of water. Should the mixture set to a gel during the titration it will prove advisable to dilute the acid still further and to carry out the titration more rapidly.

Acetic Acid.—A two-normal solution should be prepared by ordinary methods.

Distilled Water.—Best results have been secured in our laboratory with recently boiled distilled water. The chief difficulty appears to be due to the carbon dioxide, and in ordinary distilled water no trouble will be experienced.

THE EFFECT OF TEMPERATURE UPON THE TIME OF SET: THE ENERGY OF ACTIVATION

If the time of set of a certain standard gel mixture is observed as a function of temperature, the great effect of higher temperatures in hastening the setting will be evident. The experiment described was devised from the work reported by Hurd and Miller (*2*). Acetic acid is used because the hydrogen-ion control is very nearly exact.

By plotting the logarithm of the time of set against the reciprocal of the absolute temperature and by making certain assumptions, one can obtain an energy value for the reaction analogous to the energy of activation for an ordinary chemical reaction. It is particularly interesting that this value should fall within the limits for ordinary chemical reactions. The one obtained in the long series of studies reported is 16,600 calories.

In this experiment each variable except the temperature is kept constant. Several different mixtures of solutions of sodium silicate and acetic acid are made and thermostated at different temperatures. The time of set is determined for each mixture.

A number of small stirring rods, each 10 cm. long, should be made from 3-mm. glass rod. They are drawn out to a short, stubby point on the lower end and fire-polished. A number of 100-cc. pyrex Griffin beakers and watch glasses to cover them will be needed. Several ordinary water thermostats are necessary. Electrically controlled baths at 25°C. and from 40°C. to 50°C. will prove satisfactory. A mixture of wet snow and a little water will prove excellent for 0°C.

Measure 25 cc. of the silicate solution into a number of clean, dry 100-cc. beakers. Place the partly filled beakers in the 25°C. thermostat, covering them with watch glasses and weighting them to hold the beakers

down. Measure also 25 cc. of the acetic acid solution into other 100-cc. beakers, and to each add 30 cc. distilled water. Place the covered beakers in the thermostat. Allow the beakers to remain in the thermostat until a test sample in another beaker reaches and remains at 25°C. Remove one beaker of the silicate and one of the acid-water mixtures from the thermostat. At a definite time, recorded in the notebook, *pour the silicate quickly into the acetic acid* and mix thoroughly by pouring back and forth. Do not attempt to stir, since mixing can be accomplished more satisfactorily by pouring. The mixture should be clear and transparent. Place the beaker containing the 80-cc. mixture back in the thermostat, and cover it with a watch glass. Observe it from time to time until a faint but definite opalescence appears. Then test at intervals for time of set by thrusting the testing rod into the mixture at an angle of about 20° to the vertical. The bottom of the rod should touch the bottom of the beaker. The gel is said to be set when the rod just fails to fall over. With practice, an operator can determine time of set with less than 2% deviation. While waiting for the one gel to set, the operator may mix several more. As an indication, this mixture in our laboratory requires about two hours to set.

Several different mixtures should be employed, each, however, containing 25 cc. silicate solution and having a total volume of 80 cc. Satisfactory mixtures will be found to contain 20 cc., 25 cc., and 30 cc. of the acetic acid solution. Several samples of each mixture should be run in each of the thermostats.

The data should be plotted as logarithm of time of set as ordinates, either in seconds or minutes, against reciprocal absolute temperature as abscissas. The curves should be linear and those for different mixtures should be parallel. By making certain simple assumptions, namely, that in these mixtures with a constant concentration of silica, the "time of set" represents the time required for a certain definite fraction of the complete reaction and also that we may apply the methods of treatment used for ordinary chemical reactions, we may obtain an energy quantity analogous to the "energy of activation." This is obtained by multiplying the slope of the curve by 2.30 R. The value is approximately 16,600 as reported by Hurd and Miller (*2*). This article should be consulted for any further details. Ordinary students in our physical chemistry laboratory obtain values between 16,000 and 17,000 calories.

Although the exact mechanism of setting is not as yet understood, there is considerable evidence available which leads us to suspect that the molecules of orthosilicic acid are condensing, by the splitting out of water, into a meshwork structure which holds the water in close restraint. We are apparently measuring here the energy of activation of a slow stage somewhere in this process.

HYDROGEN-ION CONCENTRATION AND TIME OF SET

The effect upon the time of set of these gel mixtures caused by a change in the concentration of acid was shown by Holmes (*3*). The specific effect of the hydrogen-ion concentration upon the time of set has been shown by Hurd, Raymond, and Miller (*4*).

The same solutions of sodium silicate and acetic acid are necessary, together with a 25°C. thermostat. To measure the hydrogen-ion concentration, we have used a quinhydrone potentiometer, Leeds and Northrup No. 7654. A platinum wire electrode, No. 26 wire, is more easily cleaned than the gold electrode. It is cleaned by immersion in a strong, hot solution of sodium hydroxide and rinsed carefully with distilled water.

Place 50 cc. of the silicate solution in one 100-cc. beaker, covered with a watch glass, in the thermostat. In another beaker, preferably a 250-cc., place 50 cc. acetic acid solution and 60 cc. distilled water. Immerse in the thermostat until the temperature is constant. Have another 100-cc. beaker handy. Note the time and pour the silicate quickly into the acetic acid-water mixture in the 250-cc. beaker. Mix rapidly by whirling the solution in the beaker and pouring back and forth between the larger and smaller beaker. Finally pour half into each of the 100-cc. beakers. Cover one and place in the thermostat to be tested for time of set. Place the other beaker containing half (80 cc.) of the mixture in the same or another 25°C. thermostat and determine the pH by the quinhydrone method. Add a fair sized pinch of solid quinhydrone, stir thoroughly with a small glass stirring rod until the excess solid sinks, then introduce the platinum wire electrode and the arm of the calomel cell and adjust the instrument. This method has been shown to give a satisfactory result for the hydrogen-ion concentration in the presence of silicic acid gel (*5*).

It is necessary to make a series of mixtures here in order to vary the pH. The following volumes of acetic acid solution will be found satisfactory: 40 cc., 50 cc., 60 cc., 70 cc., 80 cc., each with correct amount of distilled water. Note, of course, that we are using double quantities so that the chemicals added in finding the pH of one half cannot affect the time of set of the other half of the mixture.

It is recommended that either the time of set be plotted as ordinate against the hydrogen-ion concentration as abscissa or, better still, the logarithm of the time of set be plotted against pH. Thus a wider range will be covered.

The interpretation of the data given by Hurd, Raymond, and Miller (*4*) may be suggested here, namely, that the reason for the linear relation between time of set and hydrogen-ion concentration is that the hydroxyl ion acts as a catalyst in this process. This proves to be a good example for study of an apparently colloidal process which in this respect, also, follows the laws of an ordinary chemical reaction.

THE CHANGE OF SURFACE TENSION DURING GELATION

An interesting experiment was reported by Hurd and Letteron (*6*). They measured the apparent surface tension of a silicic acid gel mixture during gelation with a du Nouy tensimeter. It is certain that they were not measuring a true surface tension alone, but the tensimeter readings plotted against the time show a striking similarity to the results of Prasad, Mehta, and Desai (*7*), upon the change in the extinction coefficient during setting of silicic acid gels.

The solutions of sodium silicate and acetic acid are necessary, together with a du Nouy tensimeter. It is easier to work in a room of constant temperature than in a thermostat bath. As before, mix 25 cc. silicate solution with 25 cc. acetic acid solution and 30 cc. distilled water, pouring the silicate into the acid. Noting the time, of course, determine the reading with the tensimeter at definite time intervals until the ring will no longer become incorporated into the surface when brought back. If the data are plotted as suggested, they present a picture of the suddenness of the gelation process when once started which is very illuminating. One obtains the impression of one stage of the process going very slowly with a sudden and very rapid change resulting in the setting of the gel.

THE EFFECTS OF SOLUBLE IMPURITIES UPON THE TIME OF SET

It is possible to study the effect of certain impurities upon the time of set of these gel mixtures. The effects of certain organic impurities (*8*) and of certain salts (*4*) are reported in the literature. Some impurities have practically no effect, such as glycerin. Salts decrease the time of set.

Mixtures are made using 25 cc. silicate solution and either 20 or 25 cc. acetic acid solution. The remaining volume to make 80 cc. is made up partly of distilled water and partly of the solution of the impurity. By using a sufficiently concentrated solution of the impurity any reasonable concentration of the impurity in the final gel can be obtained. If the gel shows a curdy appearance the data may be discarded, since it is evident that the character of the gel has been altered.

References in the older literature will be found concerning the accelerating or catalytic effect of certain amines such as pyridine, methyl amine, and the like. Care should be used in interpreting such data because it was shown in the study by Hurd and Carver (*8*) that these amines change the hydrogen-ion concentration and so, naturally, affect the time of set; the stronger the amine as a base, the more the effect.

THE EFFECT OF SETTING OF THE GEL MIXTURE UPON THE ELECTROLYTIC CONDUCTIVITY

There is very little change, if any, in the electrical conductivity of the gel mixture as it sets (*9*). This is somewhat of a surprise to the student who ordinarily expects that the resistance will increase considerably.

The solutions of sodium silicate and acetic acid are required, also a 25°C. thermostat. Some form of electrolytic conductivity cell and a wheatstone bridge are necessary. The solution has a low resistance, and a troublesome capacity effect will be experienced if the electrodes are too close together. A simple and satisfactory cell may be made from an ordinary 8″ test-tube. Two small platinum electrodes are mounted on glass tubes held in a two-hole rubber stopper. The electrodes should be as far apart as possible. They may consist, if necessary, of a coil of about two inches of platinum wire. It is best that they be platinized. In the work reported (*9*) a 1000-cycle alternating current from a vacuum tube oscillator was employed with a Leeds and Northrup bridge. At this frequency, a capacity balance must be used. We have since used a 60-cycle alternating current galvanometer with more success. At the low frequency, no capacity balance will be required.

The student firmly expects a large decrease in the electrical conductivity when the gel sets, just as he observes a great change in the gross viscosity. This is the best and simplest experiment of which I am aware to show to the student that the ions in a gel encounter no more difficulty in passing through the relatively large spaces in the gel structure than they do in an ordinary solution. If the ions migrate as easily through the gel as through a liquid solution, both under the influence of an electromotive force, they will presumably migrate as easily through the gel as through the liquid solution in the absence of an electromotive force. Since many portions of our bodies are composed of gel-like structures and since in general these structures are permeable to ions or to dissolved substances whose molecules are of ordinary molecular size, the observation by the student of the ease with which ions and molecules pass through these gels is important.

If the student will also study the migration into a gel, for which purpose a silicic acid gel will serve very well, of various dissolved materials, he will gain considerable information concerning the size of the dissolved particles. To list only a very few substances, the hydrogen and hydroxyl ions (both migrating into a gel already colored by an indicator) the copper ion, and several dyes such as phenolphthalein, methyl orange, and Congo red will give an excellent series to show great change in velocity of penetration. These experiments are described in a number of books and articles.

SUMMARY

A description is given of several new experiments involving the formation of silicic acid gels.

In one experiment the student can determine the energy of activation of the process by measuring the time of set as a function of the temperature.

The time of set of acid gel mixtures will be found to be proportional to the hydrogen-ion concentration.

The electrolytic conductivity of the gel mixture will be found to remain practically constant as the gel sets.

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(9) HURD, C. B. AND SWANKER, H. J., "The electrical conductivity of silicic acid gel mixtures during gelation," *J. Am. Chem. Soc.*, **55**, 2607 (1933). *See also* UPADHYDA, R. K. AND PRASAD, M., "Electrical resistance of gel forming mixtures during setting," *Current Sci.*, **2**, 216 (1933).

MOLECULAR WEIGHT OF CARBON DIOXIDE

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THE purpose of this experiment is to determine the molecular weight of a water-soluble gas by making use of the Avogadro volume. It may be used as a class demonstration or as a special experiment for those students who are ahead of the class or wish to do extra experiments. These students are sometimes a problem to an overworked teacher. The laboratory part of this experiment was performed by such a student, Mr. Robert Urmston.

The method is an evolution method and consists in evolving a water-soluble gas, carbon dioxide, which displaces an equal volume of air, which in turn displaces an equal volume of water. The carbon dioxide is obtained by heating a carbonate and the weight of the carbon dioxide is obtained by weighing the tube containing the carbonate before and after heating. The volume of the gas evolved is obtained by weighing the water displaced.

An attempt was made to find a carbonate which would not give off water upon heating and which would decompose at a moderate temperature. After trying several carbonates the conclusion was reached that this was not feasible. Those carbonates which evolve only carbon dioxide decompose at temperatures close to the softening point of glass, while those that decompose at lower temperatures seem to be hydrated carbonates or mixtures of carbonates and hydroxides or are basic carbonates.

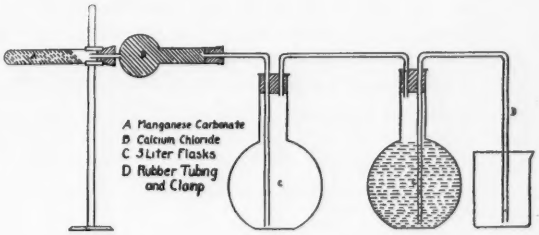
Then it was reasoned that possibly the water was evolved at a lower temperature than the carbon dioxide, thus making it possible to first prepare the carbonate by driving off the water before using the substance in the experiment. To test this idea a small electric furnace was made, consisting of a nichrome wire wound around a large pyrex test-tube and connected in series with a variable resistance. The carbonate, a thermometer, and a lead-off tube (which passed into some calcium hydroxide solution) were placed in a smaller tube which in turn was inserted into the larger tube wound with wire. In the case of manganese carbonate, moisture came off continually from 230° up to the softening point of glass, while the carbon dioxide was first evolved at approximately 243°. Consequently, the water could not be driven off without the carbon dioxide coming with it.

Referring to the order of events, the drying tube and test-tube plus the carbonate are weighed and then the apparatus is set up according to the diagram. The temperature is obtained by placing a thermometer in the first flask and the barometer is read. The apparatus is tested for leaks by blowing in the exit tube and then letting water siphon out. If any leaks are present, the water will continue to flow out of the siphon. The level of water in the beaker is made the same as that in the flask by raising the beaker, and after time has elapsed for the pressures to equalize, the pinch clamp is closed. The water is emptied from the beaker and the beaker is weighed, replaced under the exit tube, and the clamp opened. Heat the carbonate in the tube until approximately 1500 cc. of water has siphoned over into the flask. To obtain this amount of carbon dioxide about ten grams of manganese carbonate will have to be heated.

When a goodly portion of water has been siphoned over, stop heating the tube, and let the apparatus return to room temperature. Equalize the levels of water as before, and close the clamp. Weigh the beaker and water and thus obtain the volume of the carbon dioxide. Again, weigh the tube containing the carbonate and also the drying tube, thus obtaining the weight of the carbon dioxide.

SPECIMEN STUDENT DATA

Wt. drying tube, test-tube, $MnCO_3$	*Wt. drying tube, test-tube, MnO*	*Wt. (g.) CO_2*	*Vol. (cc.) CO_2*	*P (mm.)*	*Temp.*	*Mol. wt.*
93.189	91.522	1.667	960	746	21°	42.6
94.704	92.429	2.275	1309	731	17°	43.1
80.083	77.875	2.208	1245	740	21°	44.0
79.846	77.839	2.007	1143	739	23°	43.8



PROFICIENCY *of* FIRST-YEAR STUDENTS *in* QUANTITATIVE EXPERIMENTS, II

BRUCE S. FARQUHAR WITH FRANCIS EARL RAY

The University of Cincinnati, Cincinnati, Ohio

OUR previous paper embodying part I of the present title[1] has elicited several comments. One writer states that he has accumulated considerable data and hopes to get it organized soon so that it may be compared with ours. A second letter states that by placing such over-emphasis on laboratory technic the student gets a narrow mechanical conception of science. A third writer informs us that our standards are rather low, as his students are much more accurate in similar quantitative experiments. We have been asked, also, if we had data on other quantitative experiments, and the present paper is in answer to this request.

In the course in elementary chemistry at the University of Cincinnati the laboratory periods are three hours in length. An average of one-half hour is taken up in discussion of the work and in short written quizzes. Twenty-six to thirty experiments are performed, of which eight or nine are quantitative. Of the quantitative experiments about half are in the nature of "unknowns."

The results reported in the present paper cover some of these "unknowns."

In addition to showing the proficiency of the undergraduate, an analysis of the results indicates the suitability of the compound for its purpose.

THE FREEZING POINT OF A PURE SUBSTANCE: LATENT HEAT

Five substances were given out as follows.

$Na_2S_2O_3 \cdot 5H_2O$ (*Figure 1*).—A test-tube half filled with the crystalline material is heated in a beaker of water until the substance melts. The material is allowed to cool with a thermometer bulb immersed in it. When the temperature has dropped fifteen degrees the melt is seeded. As the material solidifies, the heat of fusion causes the temperature to rise to the true freezing point, 48°. Of forty-one undergraduates, twenty-three, or fifty-six per cent., came within one degree of the correct value. Twenty-eight, or sixty-eight per cent., came within two degrees. Only four, or seven per cent., failed to obtain values within three degrees. The principal source of error is heating the substance at too high a temperature while melting it. This drives off some of the water of crystallization and causes the material to freeze at a lower temperature.

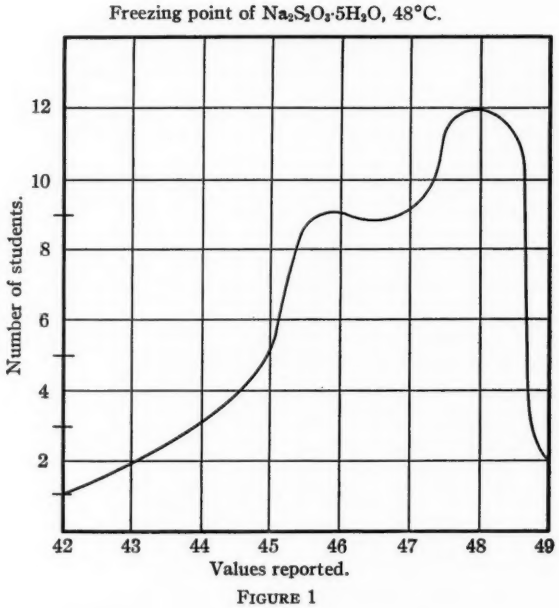


FIGURE 1

$Cd(NO_3)_2 \cdot 4H_2O$ (*Figure 2*).—Of thirty-eight undergraduates, nine came within one degree. This is not quite twenty-four per cent. Nineteen, fifty per cent., came within two degrees of the correct value, 59°. In this case thirteen persons, or thirty-four per cent., failed to secure values within three degrees. As the various samples were distributed at random, it is obvious that this substance is not very satisfactory for a freezing-point determination.

$Co(NO_3)_2 \cdot 6H_2O$ (*Figure 3*).—The results with this compound show that five of the twenty undergraduates came within one degree of the correct value, 55°. Nine came within two degrees. This was forty-five per cent. Twelve, or sixty per cent., came within three degrees. Four high values were reported (60–63°). Overheating may have driven off water and formed a lower hydrate. An additional four persons reported

[1] J. CHEM. EDUC., 13, 74 (1936).

low values (47–51°). This compound is also less satisfactory than sodium thiosulfate.

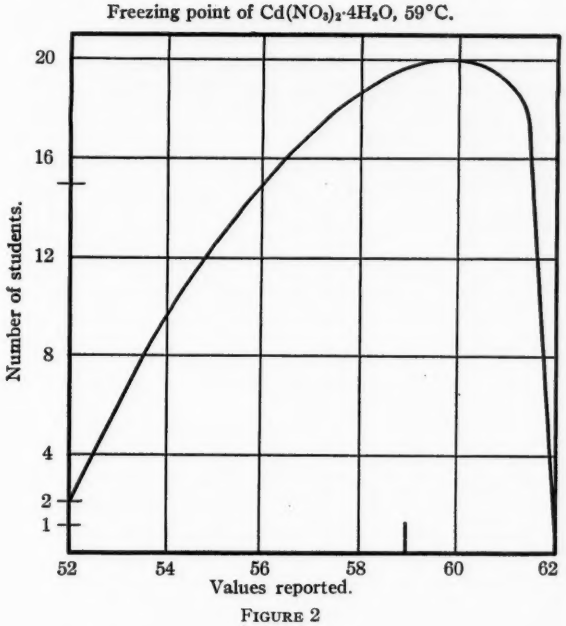


FIGURE 2

$Fe(NO_3)_3 \cdot 9H_2O$ (Figure 4).—Fourteen undergraduates worked on this determination. Seven, or fifty per cent., came within one degree; one additional report was within two degrees; ten, or seventy per cent., reported values within three degrees of the correct value, 47°. This is a very satisfactory substance to use for freezing-point determinations, as the careful student obtains very good results.

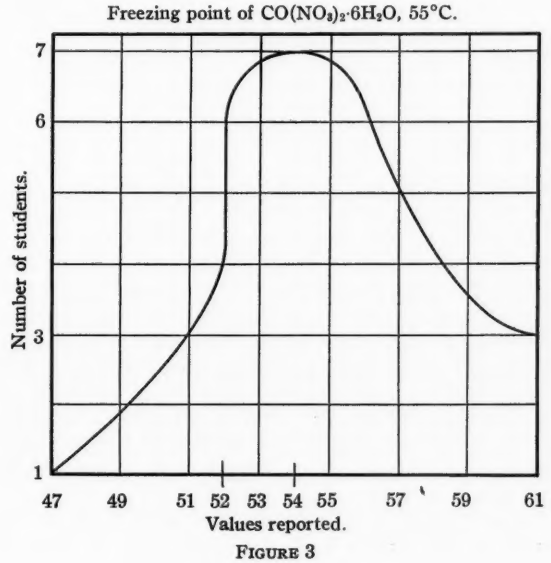


FIGURE 3

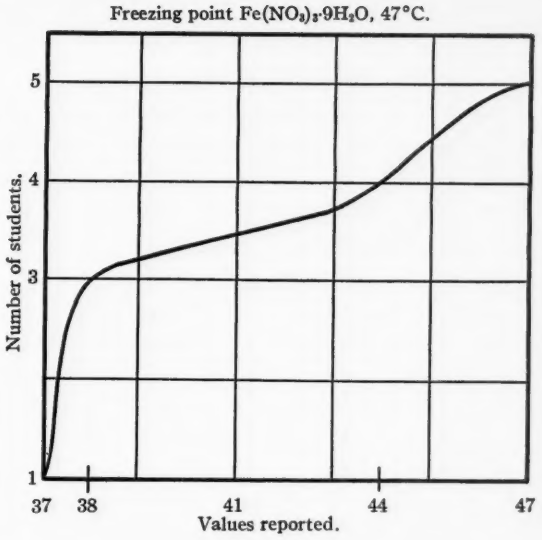


FIGURE 4

$Ca(NO_3)_2 \cdot 4H_2O$ (Figure 5).—The total number of determinations was twenty-seven. Thirteen, or forty-eight per cent., were within one degree, eighteen, or sixty-seven per cent., within two degrees, and twenty-five,

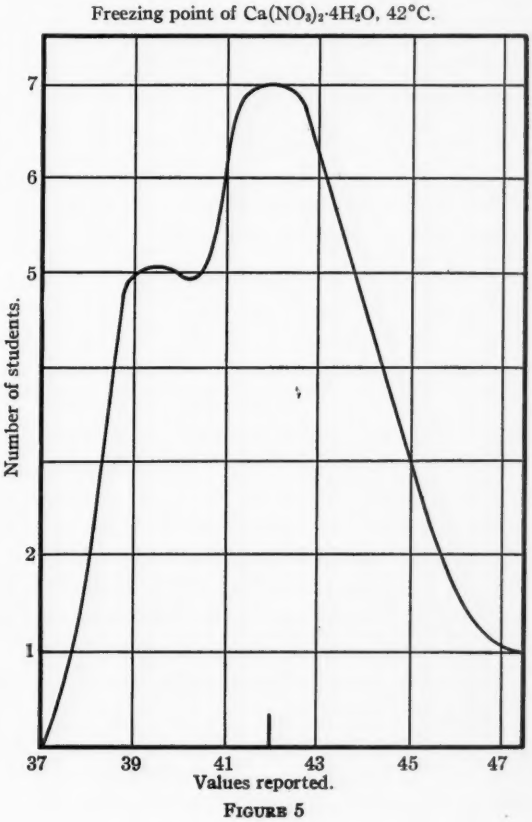


FIGURE 5

or ninety-three per cent., within three degrees of the correct value, 42°. This compound also falls within the class of satisfactory substances.

ANALYSIS OF A HYDRATE

A weighed amount of the hydrate was heated to constant weight. When the percentage of water was reported, the student was told the name of the compound. He then calculated the number of molecules of water per molecule of salt.

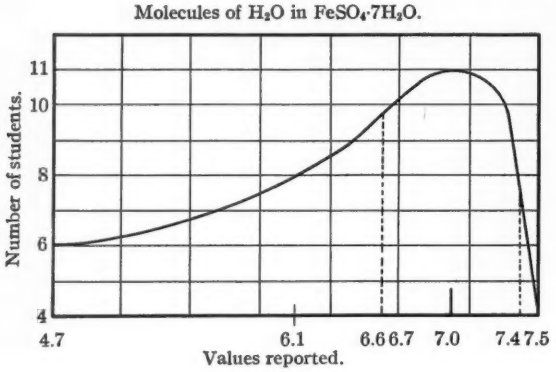


FIGURE 6

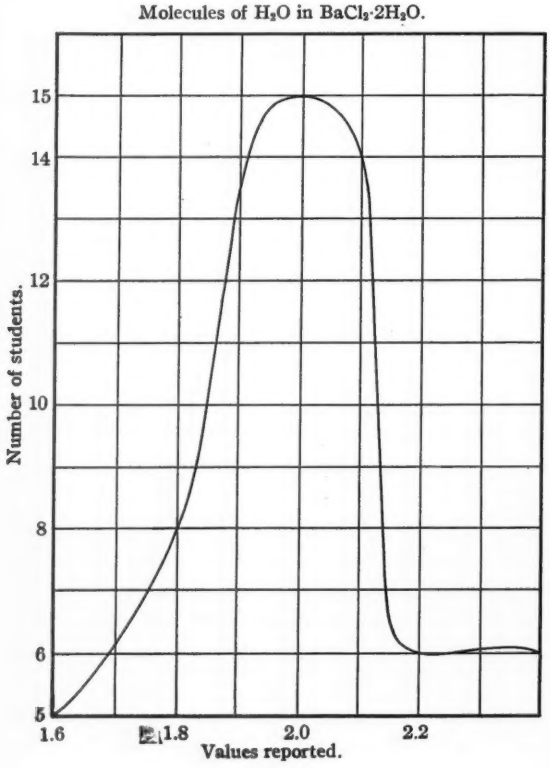


FIGURE 7

$FeSO_4 \cdot 7H_2O$ (*Figure 6*).—Values between 6.6 and 7.4 may be considered as satisfactory. Of the thirty-eight undergraduates, twenty-three, or fifty-nine per cent., came within these limits. A comparison with the results reported in our previous paper for the "known" compound $CuSO_4 \cdot 5H_2O$, in which but three per cent. of the undergraduates failed to come within similar limits seems significant and will be discussed later. The principal source of error would seem to be the oxidation of ferrous to ferric iron. This is quite superficial if a low flame is used and the sample kept partially covered.

$BaCl_2 \cdot 2H_2O$ (*Figure 7*).—Of the forty undergraduates that reported values for this compound, all came within the limits 1.6 to 2.4. In addition twenty-nine students, seventy-two per cent., came within 1.8 to 2.2 mols. of water. Apparently this compound is almost fool proof, because of the low water content and the stability of the anhydrous salt.

SPECIFIC HEAT: LAW OF DULONG AND PETIT

Lead (*Figure 8*).—Various values for the specific heat of lead have been recorded in the literature. Probably the most recent and reliable figures are those of Wüst, Meuthen, and Durrer. At 0°C. they give a value of 0.0359, and at 100°C. a value of 0.0336. This gives as an average value 0.0348, which is probably as satisfactory as any. In this connection it is interesting to note that the maximum of our curve is at 0.036. Nineteen of the thirty reports, or sixty-three per cent., came within the limits 0.031 and 0.038 which represents a ten per cent. error. Six fell below, while five exceeded these limits.

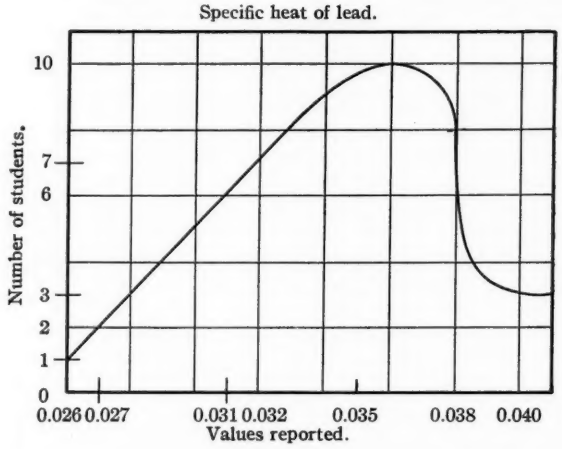


FIGURE 8

Antimony (*Figure 9*).—Sixteen of the twenty reports, eighty per cent., came within the limits 0.043–0.050 which represents a ten per cent. error. None fell below this limit.

Iron (*Figure 10*).—While the best value in the literature for the specific heat of wrought iron is close to

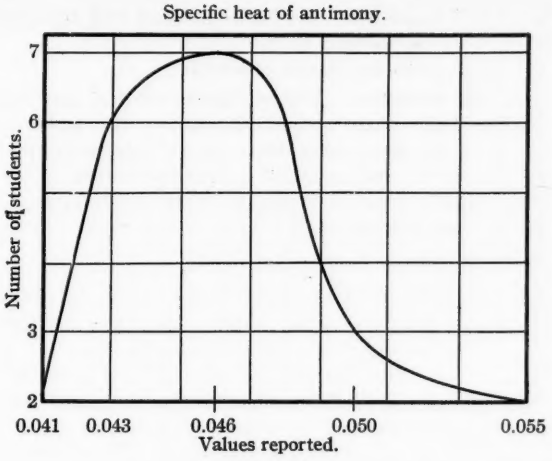


FIGURE 9

0.11, we have selected 0.12 and allowed a deviation of ten per cent. from this. Probably the bar of iron used was not of high purity. Of thirty-five reports, twenty-six, or seventy-four per cent. were within the ten per cent. limits of 0.11 and 0.13. Six values were low, while three were high.

DISCUSSION

A comparison of the per cent. of error in the analyses of the known materials, Part I, and the per cent. of error in the determinations on "unknowns" given in the present paper shows that the variation is much greater in the case of the "unknowns." There seem to be three reasons for this. The first, "doctoring of results," need not be discussed here. The second, a psychological feeling of uncertainty in venturing into the unknown, should be recognized, and an effort should be made to dispel it in the talk preceding the experiment.

The third and most important reason for the larger error on "unknowns" is inherent in matter itself. As each substance must differ in property from all other substances, so it is impossible to give as precise directions for a group of substances as for a single substance.

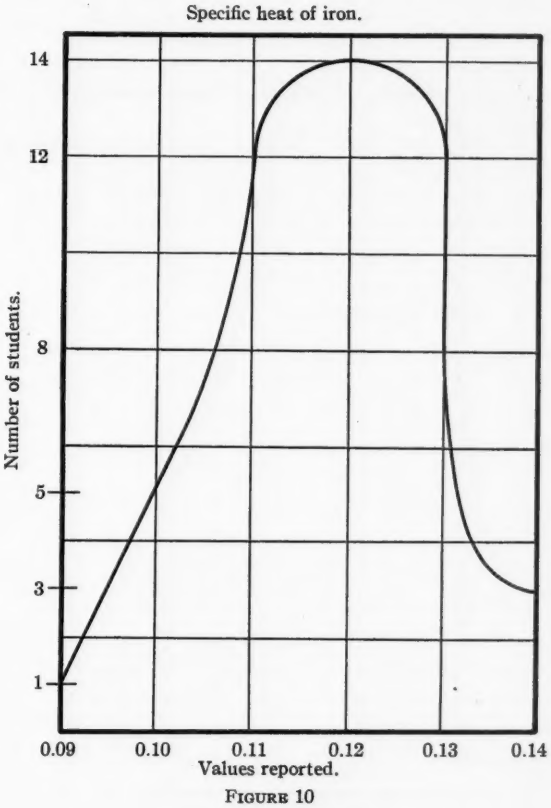


FIGURE 10

As chemistry is an experimental science whose *raison d'etre* is exploring the unknown, it is very important that the qualities of initiative, adaptability, and resourcefulness be encouraged and developed whenever discovered. This, we feel, is accomplished by working with carefully selected "unknowns."

The PHOTOGRAPHIC CLUB

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A SMALL but well-organized photographic club may be a valuable addition to the list of student extracurricular activities in many high schools and colleges. As a project it will appeal particularly to advanced students enrolled in courses in chemistry and physics. The following suggestions may be helpful to those supervising the activities of such a club or contemplating photographic work in connection with regular class work.

Purpose: Organized for the purpose of stimulating an interest in photography and as a means of learning the basic chemical and physical principles involved in photographic work.

Organization: The following items must be decided.

1. How to start the club.
2. Who may become members.
3. How the members shall be selected.
4. When and how often the club will meet.
5. When the members can do individual work.

Equipment needed:

1. Darkroom. (Paint with black window screen paint.)
2. Supply of films, plates, and photographic paper.
3. Chemicals.

a. Essential.	*b. Desirable.*
Acetic acid	Citric acid
Amidol	Chrome alum
Borax	Ferrous sulfate
Elon (Metol)	Formalin solution
Ferric ammonium citrate	Glycerin
Hydroquinone	Hydrochloric acid
Hypo	Mercuric chloride
Potassium alum	Potassium bichromate
Potassium bromide	Potassium ferricyanide
Pyro	Potassium oxalate
Sodium bisulfate	Potassium permanganate
Sodium carbonate	Silver nitrate
Sodium hydroxide	Sulfuric acid
Sodium sulfite	Wood alcohol

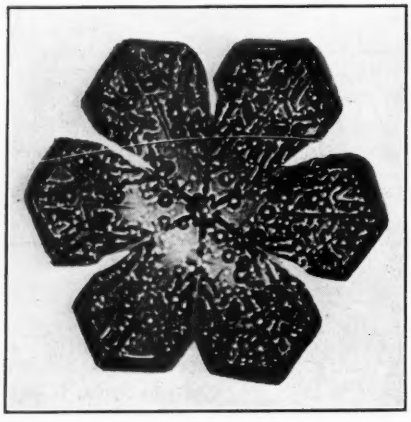

FIGURE 1.—REPRESENTATIVE MICROPHOTOGRAPH OF SNOWFLAKE

(The desirable list includes those chemicals that are used in more advanced practices such as reduction and intensification.)

4. Accessories.
   - 1 camel's-hair brush
   - 1 centigrade thermometer
   - 2 film clips (numerous substitutes may be used)
   - 1 graduated cylinder
   - 1 negative drying rack (for plate work only)
   - 1 negative washer (desirable but substitutes may be used)
   - 1 print washer (desirable and may be homemade)
   - 3 trays (each should be marked and used for one solution only)
   - 1 trimming board (desirable)
5. Safety lights. A brown salt bottle and showcase bulb makes a good substitute. Red paper or cellophane may be used for additional protection when handling films and plates.
6. Printing box. (This may also be used as a retouching stand.)
7. Books.

"The British Journal Photographic Almanac," Henry Greenwood and Company, 24 Wellington Street, London, England.

CHARLES, DAVID, "Commercial Photography," Sir Isaac Pitman Company, New York City, 1928.

COLLINS, A. F., "The Amateur Photographer's Handbook," Thomas Y. Crowell Company, New York City, 1925.

DAVIS, W. S., "Practical Amateur Photography," Little, Brown & Company, Boston, Massachusetts, 1923.

Mallinckrodt Chemical Works, "Chemistry of Photography," Mallinckrodt Chemical Company, St. Louis, Missouri, 1931.

NEBLETTE, "Photography, Its Principles and Practice," D. Van Nostrand Company, New York City, 1930.

"Photography without Failure," American Photographic Publishing Company, Boston, Massachusetts, $1.25.

ROEBUCK, J. R., "The Science and Practice of Photography," D. Appleton & Company, Boston, Massachusetts, 1917.

STRONG, WILLIAM M., "Photography for Fun," Leisure League Little Book Number 7, 25 cents.

WATKINS, ALFRED, "Photography, Its Principles and Practices," Constable & Company, London, England, 1920.

Eastman Kodak Company, Rochester, N. Y.
- "About Lenses."
- "Book of Formulas."
- "Collodion."
- "Color Films."
- "Commercial Photo Finishing."
- "Elementary Photographic Chemistry," 50 cents.
- "The Fundamentals of Photography," $1.00.
- "How to Make Good Pictures," 50 cents.
- "Lantern Slides—How to Make and Color Them."
- "Picture Taking at Night."
- "Plates and Filters."
- "Printing."
- "Professional Enlarging and Equipment."
- "Professional Equipment."
- "Reproduction Work."
- "X-rays."

8. Magazines.
   American Photography (Monthly), 428 Newbury Street, Boston, Massachusetts, $2.50.
   Camera Craft (Monthly), Camera Craft Publishing Company, Claus Spreckels Building, San Francisco, California.
   Kodakery (Monthly), Eastman Kodak Company, Rochester, New York, 60 cents.
   Photo Art Monthly (Monthly), Photo Art Publishers, Monadnock Building, San Francisco, California.
   Photo-Era (Monthly), Photo-Era Publishing Company, Wolfeboro, New Hampshire, $2.50.

Possible types of work:

1. Exposure and development of films and plates.
2. Compounding of developer and fixing solutions.
3. Prints on developing paper.
4. Prints on printing-out paper.
5. Preparation of lantern slides by contact and reduction.
6. Intensification of films and plates.
7. Reduction of films and plates.
8. Spectrum photography.
9. Microphotography. (See Figures 1 and 2.)
10. Blue prints.
11. Enlargements. (Use a slide projector for an enlarger.)
12. Toning of prints.
13. Preparation of collodion plates.
14. Photography with filters.
15. Silhouettes.
16. Color photography.
17. Carbon printing.
18. Telephoto work.
19. Infra-red photography.
20. Trick photography.
21. Flashlight photography.
22. Night photography.
23. Motion pictures.
24. X-ray photographs.

Possible results: The members of the club may learn the basic principles of any of the above types of photography, depending upon their interests and activity. With little effort they can learn the proper methods of taking a picture, how to develop plates and films, how to print pictures and develop positives, how to correct faulty negatives by reduction and intensification, a brief history of photography, and how films and photographic paper are prepared.

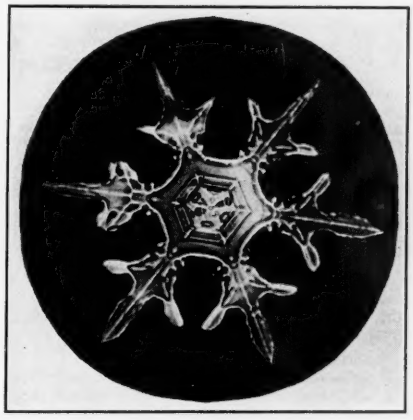

FIGURE 2.—MICROPHOTOGRAPH OF SNOWFLAKE PREPARED BY A STUDENT

The subject may prove to be a stimulus to work in chemistry and physics and a useful hobby for later life.

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For nothing is so productive of elevation of mind as to be able to examine methodically and truly every object which is presented to thee in life.—MARCUS AURELIUS

W. O. Brooks
A. T. Burtsell
R. K. Carleton
Tenney L. Davis
J. Howard Graham
B. Clifford Hendricks
J. W. Howard

ABSTRACTS

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G. H. Woollett

KEEPING UP WITH CHEMISTRY

Systematics of the chemistry and physics of the synthetic products. Anon. *Chem.-Ztg.*, **60**, 656–7 (Aug. 8, 1936).—A chemist, Dr. G. Kränzlein, proposed the following scheme at a meeting of the section on synthetic products in Munich in 1936:

Chemistry of Synthetic Products

A. General.
   1. Theoretical and comprehensive studies.
   2. Analytical and testing.
   3. Statistics, economics and laws.
   4. Bibliography, book reviews and nomenclature.
   5. Physiological.

B. Raw Materials.
   I. Synthetics from transformation of natural products.
      a. Mineral origin.
         1. Inorganic constituents.
         2. Organic constituents.
      b. Plant and animal origin.
         1. Hydrocarbons like caoutchouc, gutta-percha and derivatives.
         2. Carbohydrates like cellulose, lignin, starch, sugar.
         3. Fats, oils, waxes and resins.
         4. Proteins like casein, glue and gelatin.
   II. Synthetics from products in coal tar.
      a. By condensation.
         1. Phenol—phenol plastics.
         2. Anilin—amino plastics.
         3. Phthalic acid—alkyd resins.
         4. Hydrocarbons and derivatives of the latter.
      b. By polymerization.
         1. From styrol, cumarone, indene, cyclopentadiene, etc.
   III. Synthetics from acetylene.
      a. By condensation.
         1. Acetaldehyde—acetaldehyde resin.
      b. By polymerization.
         1. Vinyl acetate.
         2. Vinyl halogenide.
         3. Vinyl ether and thioether.
         4. Vinylamine.
         5. Ethylene polycarboxylic acids.
         6. Methacrylic acid esters (from acetone).
         7. Polymerized acetylene.
            Vinylacetylene.
            Divinylacetylene.
            Cuprene.
         8. Vinyl alkyl ketone.
   IVa. Synthetics from ethylene as raw material for polymerizations.
      1. Polymerized ethylene.
      2. Ethylbenzenes—styrenes.
      3. Ethylene chlorhydrin—ethylene oxide.
      4. Ethylene oxide—ethylene cyanhydrin—acrylic nitrile—acrylic acid—acrylic acid ester.
   IVb. Synthetics from propylene and higher olefins for polymerization purposes.
   V. Raw materials from the three most important large-scale hydrogenation processes.
      a. NH_3 synthesis: Urea—formaldehyde condensates (amino plastics).
      b. Methanol synthesis:
         1. Formaldehyde—phenol plastics, amino plastics.
         2. Isobutylene—polymerizates.
      c. Hydrogenation of coal as a source of unsaturated aliphatic compounds.

C. Uses.
   1. Plastic materials and their applications.
   2. Films, foils and threads.
   3. Impregnation with synthetic products.
   4. Synthetic leather, linoleum.
   5. Refinements of textiles by synthetic products.
   6. Glues and cements.
   7. Compounds.
      a. Compound glass.
      b. Other compounds like veneers.
   8. Surface protection and treatment.
      a. Cellulose derivative lacquers.
      b. Lacquers from chemical derivatives of caoutchouc.
      c. Oil lacquers.
      d. Alcoholic lacquers.
      e. Emulsion lacquers.
      f. Lacquers from other raw materials.
      g. Combination and special lacquers.
      h. Miscellaneous and removal of lacquers.
   9. Architecture.
   10. Electrical industry.
   11. Other applications.

D. Assistants for synthetic products.
   1. Catalysts.
   2. Stabilizers.
   3. Drying agents.
   4. Solvents and softening agents.
   5. Dispersing and thickening agents.
   6. Dyes and brightening agents.
   7. Fillers and pigments.

E. Progress in mechanical devices.

Another classification is described which is based entirely on physical properties and which has been proposed by Dr. Richard Vieweg. L. S.

How the synthesis of caoutchouc originated. F. Hofmann. *Angew. Chem.*, **60**, 693–6 (Aug. 22, 1936).—An interesting and detailed historic review by the inventor of artificial caoutchouc as made from the gas butadiene. L. S.

The photochemical reactions of halogens with organic compounds of the aliphatic series. H. J. Schumacher. *Angew. Chem.*, **49**, 613–7 (Aug. 15, 1936).—The photochemical reactions of halogens with aliphatic compounds are thoroughly discussed, accompanied by numerous equations. It is shown that the transformations of C—H into C-halogen compounds and that from C=C and C≡C into $\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}$ and $\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}$ take place in a similar manner. The reactions are of the chain type, the chains being of considerable lengths. They are characterized by the formation of primary halogen atoms which form radicals by reaction with the hydrocarbon. If C—H compounds are halogenated HCl is formed and also a radical containing trivalent C. In the case of C=C and C≡C compounds the halogen is absorbed with the simultaneous splitting of the double and triple bonds, thus forming new radicals. By reaction of the latter with the halogen molecule the halogen atom is re-formed, which thus continues the chain by producing the corresponding halogenation products. Each reaction which absorbs a chain carrier, *i. e.*, a halogen atom or a radical, without re-forming the latter completes the chain. The chain-disrupting reaction differs in the various cases, and influences the quantum yields and also the velocity equation. The occurrence of similarly constructed radicals in the various reactions requires that they be similar not

only kinetically, but also chemically. The presence of oxygen is particularly characteristic. If present in low concentrations, oxygen retards the halogen reaction, while if the concentrations of oxygen are higher, sensitized oxidations occur. Various quantitative reactions are discussed critically and their reaction mechanisms are shown. Molecules of the form Cl_3 and Br_3 are not produced in these reactions. The influence of the solvent is discussed. L. S.

The inhibition of roots by growth hormone. R. H. LANE. *Am. J. Botany*, **23**, 532–5 (Oct., 1936).—Indole-3-acetic acid is a specific inhibitor of the growth of roots of young *Avena* seedlings. Some thickening of the roots occurs but not enough to account for the decrease in length.

The sensitivity of the roots is sufficiently great for the technic to be used for a quantitative assay of growth hormones.

The number of roots is increased by treatment with this acid. E. D. W.

Social significance of air pollution. H. B. MELLOR. *Ind. & Eng. Chem.*, News Edition, **14**, 411–2 (1936).—Water and food have been made safe for human consumption as a result of efforts of the chemical, medical and engineering professions, but the problem of making air hygienically safe is only now being attacked. The only satisfactory way to achieve a solution is to control the pollution at the source of trouble. The social significances of air pollution are discussed and future plans are discussed to obtain adequate information concerning methods of purification, so that a sound program of municipal and industrial control of air pollution may be established. A. A. V.

APPARATUS, DEMONSTRATIONS, AND LABORATORY PRACTICE

Cleaning steel—chemically. R. L. DAVIES. *Chem. & Met. Eng.*, **43**, 606 (Nov., 1936).—Steels must be thoroughly cleaned before the application of protective coatings, films, and enamels.

Anhydrous sodium orthosilicate is rapidly finding its place among the industrial alkalies for this purpose. Its action is aided by brushes, wiping rolls, pressure sprays, and electrolytic machines. J. W. H.

SCIENTIFIC REVIEWS AND BIBLIOGRAPHIES

Chemicals used for the alleviation of pain. C. ROHMANN. *Chem.-Ztg.*, **60**, 713–6 (Aug. 29, 1936).—The following types are discussed and formulas for some of the chemicals described are given below:

1. *Inhalation narcotics:* dichlormethane, chloroform, ethyl chloride, ethyl bromide, divinyl ether, ethylene (C_2H_4) or acetylene (C_2H_2) mixed with oxygen, laughing gas.
2. *Complete narcotics:* avertin, rectidon, various barbituric acid derivatives, evipan *N*, eunarcon.
3. *Opium alkaloids and their derivatives:* morphium, codeine, heroine, thebaine, eucodal, dicodid, acedicone.
4. *Chemicals used for fighting fever and pain:* kairin, thallin, antipyrene, pyramidon, melubrin, novalgin, cocain, tropacocain, eucain *B*, stovain, alypin, methyl ester of *m*-amino-*p*-hydroxybenzoic acid, anesthesin, novocain, totocain, larocaine, diocain, percain. L. S.

THE PHILOSOPHY OF EDUCATION

Cultural and social values of science. SIR R. GREGORY, PROF. L. HOGBEN, AND SIR A. D. HALL. *Nature*, **138**, 594–6 (Oct. 3, 1936).—At the Blackpool meeting of the British Association, Section L (Educational Science) discussed the cultural and social values of science. Sir Richard Gregory stated that "when science is taught, not as an aid to a vocation, but as part of the training of a modern citizen, it may justly be claimed to have a cultural value. . . . Science and literature, or what are called the humanities, are not now regarded by responsible authorities as opposing elements in education. . . . Progress in physics and chemistry has profoundly altered those social conditions which it is the purpose of social science to study. . . . Unless science repudiates the methods of cultivated barbarism involved in modern warfare, it must lose whatever right it now possesses to be a spiritual influence. . . . Such an end . . . will be avoided by conserving social and spiritual values with scientific teaching and research. . . ."

Professor Lancelot Hogben believes that "a course of general science adapted to the requirements of citizenship should be orientated towards the elucidation of the major constructive achievements of natural knowledge in the evolution of civilization" and that such a course should include "the construction of the calendar, the technique of navigation and map making, the extension of deep-shaft mining and exhaustion of fuel supplies, the introduction of inanimate and mobile power, the discovery of chemical fertilizers and the principles of scientific breeding, the control of epidemic diseases, and the national dietetic minimum. . . ." He adds that the question as to "whether science will take its needful place in the instruction of the citizen and statesman depends far less on the attitude of the scientific specialist than on that of the educationist. . . ."

Sir A. D. Hall said: ". . . The specific value of education on a basis of science is that it will encourage if not create a habit of acting on reason rather than emotion. . . ." Politicians use false emotional issues to build up the self-delusion of belonging to a chosen race. "The function of an education based on science is to destroy this illusion and to teach people . . . that men and women, however diverse as individuals, yet are, collectively and statistically, very much alike. . . . Men of science will have to organize to make their point of view prevail. This is alien to the temperaments of the leaders in the world of science. They want to remain in their laboratories and secrete knowledge without bothering about its purpose. To do so is to accept slavery." M. E. W.

GENERAL

German chemists at Munich. ANON. *Nature*, **138**, 457 (Sept. 12, 1936).—A national congress of German chemists met at Munich, July 7 to 11. Dr. O. Nicodemus delivered an address on the chemistry of acetylene, the source of isoprene, butadiene, and chloroprene, from which synthetic rubber is made. The Congress consists of twenty sections, one of which is devoted to artificial products. Dr. O. Röhm has developed an "organic glass," which is derived from α-methylacrylic acid and is free from silicates. The esters of this acid can be polymerized to very transparent vitreous solids having a low coefficient of expansion. This glass is suitable for windows of motor-cars and airplanes, for optical purposes, and for filter-presses. An artificial resin, trolitul, with insulating properties which permit its use even with high frequencies, is made by polymerization of the hydrocarbon styrene. M. E. W.

RECENT BOOKS

AN ELEMENTARY CHEMISTRY. *A. H. B. Bishop*, Headmaster of Warwick School, and *G. H. Locket*, Assistant Master at Harrow School. Oxford University Press, New York City, 1936. 401 pp. 2 tables. 133 figs. 12 × 18 cm. $1.75.

This book is written by teachers in English schools, for use in English schools, to meet certain English examinations. Whether it successfully accomplishes the aims of the authors can best be told by teachers in English schools using it under the conditions just named.

The best that this review can do is to record the impressions that a perusal of the book makes on a teacher accustomed to American schools and methods.

Inspection of the contents shows that the topics covered are essentially the same as those common to most chemistry texts. The first two chapters deal with physical and chemical changes, mixtures, compounds, and oxygen. Chapters III and IV deal with oxides, hydroxides, acids, bases, salts, properties of salts, and solubility.

The next four chapters deal with hydrogen, water, action of metals on water, and properties of gases. Next, four chapters on theory are inserted. Then follow six chapters on carbon, carbon compounds, flame, various fuel and illuminating gases and the carbon cycle. The next four chapters deal with the air, nitrogen, nitrogen compounds, and fixation of nitrogen, followed by five chapters on other non-metallic elements. Then come four chapters devoted to electrolysis, ionic theory, hydrolysis, classification of the elements, the periodic system, oxidation and reduction, affinity table, and the electromotive series.

Chapter XXXI covers the general methods of extraction of metals from their ores, with details of production of sodium, aluminum, and iron. Then follow seven short chapters on compounds of the more common metals. The last chapter deals with volumetric analysis and is followed by miscellaneous examination questions and tables like those ordinarily found at the end of a chemistry text.

The following are random points noted by the reviewer:

The authors feel that "not enough attention has been paid to the chemical properties of the metals at an early stage," but separate paragraphs on the properties of the metals are not evident in the text.

"Manufacturing processes have been carefully considered in the light of the most recent accounts available." Most of those stressed seem to be European. The Frasch process is described in thirteen lines and has no diagram. The preparation of bromine from magnesium bromide and from sea water is not mentioned.

"The authors have constantly borne in mind the necessity of practical work. . . ." By this they apparently mean laboratory work. Directions (in fine print) for one hundred forty-six experiments are interspersed throughout the text. "Many and probably all of the experiments could be carried out as demonstrations in front of a class where material is very limited." In many cases these directions are not written up in sufficient detail to enable the student to perform the experiments profitably, although the preface states that "all practical instructions have been given in full." They serve rather as suggestions to a teacher of experience, or for the purpose of telling the student what would happen in case the experiments were performed. Furthermore, they were apparently written up hastily, as some have titles, while others do not.

In Experiment 12 on page 30, twenty-five cc. of sulfuric acid is measured out by sucking the acid up into a 25-cc. pipet—hardly a "safety-first" method for a beginning student.

An interesting instance of "balance," or emphasis on topics, is the ten pages devoted to the subject of equivalents. Directions are given for five experiments to illustrate as many different methods of determining equivalents.

The general methods of extraction of metals from their ores are different from those found in the widely used syllabi in America.

Many of the questions listed at the ends of the chapters are taken from examination papers given by seven recognized English examining bodies.

To one accustomed to see each separate chapter begin at the top of a right-hand page it is a bit confusing to find chapters following each other without any break in the set-up. It may work toward giving the student the idea of the unity of the whole, but it hardly emphasizes the units into which the whole is logically divided.

The line cuts are usually clear, but often the parts of the apparatus are not labeled. A generous number of halftones add variety, and they are pleasingly clear as to detail.

American scientists, Langmuir, Lewis, Remsen, and Richards, are not mentioned in the index, nor in the body of the text, so far as the reviewer can find.

The index is not as satisfactory as one might wish. Only a little over four pages of index does not seem to be enough to make the 400-page book handy for reference by the student.

One naturally looks in a modern book for the improved method of writing troublesome formulas, such as those for plaster of Paris and gypsum, in the manner recommended by the Committee on Labels (Division of Chemical Education, American Chemical Society), but the authors of this book should not be criticized too harshly for this omission, because American authors are not entirely blameless in this respect. It is simply another instance of not being aware of helpful teaching devices already in use.

Step equations for complicated reactions such as dilute and concentrated nitric acid on metals seem to be omitted. So, apparently, does the method of balancing equations by gain and loss of electrons. The term proton does not appear in the index, nor on page 303 which is devoted to the planetary structure of the atom. A whole chapter is devoted to oxidation-reduction, but the term electron does not appear in it.

Historical touches punctuate the book, but in places the text leaves much to be amplified by the teacher, both historically and otherwise.

Much of the purely descriptive matter, particularly in the latter part of the book, appears to be a selection and condensation from the fuller material often found in college texts. This gives it an encyclopedic flavor. The earlier parts of the book are developed more logically.

It is doubtful if many schools in this country will care to introduce this book as their regular text, but many teachers will probably wish to have a copy at hand for occasional reference, particularly as some of the experiments described are not those usually found in an elementary text.

WILHELM SEGERBLOM

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ORGANIC CHEMISTRY. *L. J. Desha*, Professor of Chemistry, Washington and Lee University. McGraw-Hill Book Co., Inc., New York City, 1936. xv + 750 pp. 43 tables. 53 figs. 13.5 × 20.5 cm. $3.75.

Professor Desha's book differs considerably from most organic texts in arrangement of subject matter. Instead of the conventional development of material beginning with aliphatic compounds, and continuing after aliphatic chemistry with the chemistry of aromatic compounds, this text treats hydrocarbons, both aromatic and aliphatic, in Part I and then continues in Part II with simple derivatives of hydrocarbons (alkyl halides, hydroxyl derivatives, ethers, carbonyl derivatives, carboxylic acids, amines, compounds of sulfur, and organometallic and related compounds). Part III treats polysubstituted and mixed

compounds. Part IV is concerned with tautomerism, rearrangements, dyes, and stereoisomerism under the heading of "Special Results of Certain Structures," while Part V is devoted to "Some Important Plant and Animal Products" (carbohydrates, fats, proteins, and miscellaneous products). A brief appendix contains a discussion of the identification of organic compounds.

We believe that the acceptance which this book receives will be determined largely by whether or not prospective users believe with Professor Desha that the arrangement of subject matter outlined above is desirable, for the book is well written, the treatment of subject is quite adequate, and the choice of material well made. The text is practically free from typographical errors, and print, paper, and binding are of high quality.

NATHAN L. DRAKE

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AN INTRODUCTION TO THE PREPARATION AND IDENTIFICATION OF ORGANIC COMPOUNDS. *R. D. Coghill and J. M. Sturtevant*, Yale University. McGraw-Hill Book Co., New York City, 1936. xiii + 226 pp. 24 figs. 14 × 20 cm. $1.75.

This manual represents an attempt to include in one year's laboratory work the main features of the usual preparative course and of the less usual but highly desirable course in qualitative organic analysis. To make this possible in practice "the student makes only half as many preparations as formerly, the remaining time being devoted to a form of qualitative organic analysis." The results of this method of instruction in the laboratory of the authors are described as "very gratifying."

The book is in two parts: Part I, preparations, and Part II, identification of organic compounds. The preparative part occupies one hundred seventeen pages, distributed thus: general instructions, nine pages, discussion of important laboratory operations, forty-one pages, and directions for preparations, sixty-seven pages. The section on qualitative analysis occupies ninety-two pages. It is followed by two appendixes, giving atomic weights, densities of some solutions, and a list of reagents for the qualitative work. There are two indexes, one for compounds made, used, or identified in the course, and the other a subject index. The first is incomplete with respect to a number of compounds listed in the tables of derivatives.

The chapter on "Important Laboratory Operations" discusses distillation, filtration, crystallization, determination of melting and boiling point, washing and drying of liquid compounds, and extraction with immiscible solvents, and gives directions for purification of some common solvents, including the drying of alcohol by sodium and ethyl phthalate. Directions are given for the laboratory preparation of hydrogen chloride, ammonia, carbon dioxide, and hydrogen sulfide. Other needed gases (chlorine, sulfur dioxide, oxygen, hydrogen, nitrogen) are to be provided in cylinders.

Among the comments of a critical nature suggested by a reading of this section are the following. The use of norite is specified for the "removal of soluble impurities," with no mention of decolorization. It would seem better to refer to decolorizing carbon, naming norite as one of the available brands. Directions for the washing of crystals on a suction filter leave the student free to add the wash-liquid with the suction on. The purification of acids and bases by dissolving in water as their salts, treating with decolorizing carbon, and then reprecipitating, is referred to as recrystallization.

The presentation of the subject of stem corrections in melting- and boiling-point determinations may be justified on the ground that the degree of accuracy sought is not high, but scarcely on didactic or scientific grounds. The usual formula for the calculation of the stem correction is given, with a curve which shows the magnitude of the corrections from 50° to 300°, the average temperature of the exposed stem being in some unexplained way kept at 25° through the whole temperature range. Both are then ignored, and a curve for the composite stem and calibration corrections is empirically obtained for the thermometer by the boiling-point method using a 50-cc. side-arm flask. The same corrections are presumably to be applied to boiling points and melting points taken in flasks of other shapes and sizes. No auxiliary thermometer is used, and the discussion gives the impression that the average temperature of the exposed stem is the same as room temperature. No mention is made of short-scale total-immersion thermometers. It is in fact stated that to secure total immersion is "obviously impractical." This treatment of the important matter of corrected thermometric readings is not consistent, in the opinion of the reviewer, with the "vigorous protest" lodged in the preface "against the prevalent practice of cluttering up the chemical literature with 'uncorrected' melting and boiling points—figures without any great significance, which could just as well have been corrected and presented in the literature as reliable data." In the directions for the melting-point determination the reference to the temperature "at which melting starts" will probably be misinterpreted by many students. The definition of the melting point is followed by an account of the capillary tube method, the inference being that this procedure determines the true melting point as stated in the definition. The section on laboratory operations includes no mention of methods used for drying organic solids.

The preparative section describes forty-two experiments, of which "only a fraction can usually be included in any course." The list of experiments covers the usual ground in satisfactory manner, illustrating the more important reactions and methods. To perform only a fraction of the experiments, however, might give the student a decidedly limited acquaintance with preparative "techniques."

Several of the preparations may be welcomed as desirable new student experiments, *e. g.*, ethyl resorcinol and *p*-bromophenacyl bromide. The number of virtual duplicates seems high for so restricted a list, but this feature will permit a wider range of choices while affording all members of a class the same essential experiences. A number of experiments require distillation under reduced pressure. Liquid bromine is used in at least four experiments and gaseous chlorine in two, but the student, exposed to these hazards, is instructed to discard his trace of cuprous acetylide as "dangerously explosive" and is thus denied the pleasure of exploding it. There is no experiment on the carbohydrates, none on fractional distillation, and no example of a hydrocarbon synthesis.

Each experiment is preceded by a statement regarding the method to be used, or alternative methods. These sections are usually very brief, with the first sentence in many cases conveying the information that the method is important, common, typical, or convenient. No tests are applied to the compounds prepared to verify their chemical characteristics, although in the present manual such tests would seem to be more than ordinarily helpful, as an approach to the analytical work. Each experiment is followed by a number of well-chosen questions, to be answered in the laboratory notebook.

In the experiment on acetyl chloride the compound $P(OCOCH_3)_3$ is stated to be a typical by-product, but is not among the products revealed in Brooks's study [*J. Am. Chem. Soc.*, **34**, 492 (1912)] of the reactions between acetic acid and phosphorus trichloride. In the experiments on preparation of ethyl bromide no mention is made of ether as a by-product. The apparatus shown for preparation of ethylene and that for ether both have rubber connections inside the reaction flask. "Final purification" of acetamide is effected by addition of ether to the molten crude product, all flames within ten feet being extinguished! Acetanilide is made by acetylation with acetic anhydride in water, and the student is left to infer that the other acetylating agents mentioned in the introductory paragraph (acetyl chloride, acetic acid, ketene) could be used in a similar manner. No mention of the usual method of acetylation appears until it is given in the qualitative part for preparation of acetyl-derivatives of amines. The diazo-reaction is well represented by four experiments. There is one Grignard synthesis, and opportunity for other applications in the qualitative section. Glycine, made from chloroacetic acid, is isolated by the old copper glycine

method. Hippuric acid is made physiologically as an example of detoxification in the body, an experiment that always interests students. The benzoin-benzil-benzilic acid experiment is a doubtful choice for inclusion in a curtailed preparative course. It contains references to pinacone and pinacoline, names no longer considered desirable. The preparation of benzyl chloride and that of anthranilic acid both require chlorine gas, which is in any case hazardous and, if a cylinder of liquid chlorine is not available, decidedly inconvenient. There appears to be no good reason why bromine should not be used in these experiments. The student would readily understand why chlorine is used industrially, and why the substitution was made for his laboratory work. The preparation of ethyl resorcinol illustrates well the Nencki condensation and the Clemmensen method of reduction. The experiment on diphenylthiourea, phenylisothiocyanate and triphenylguanidine, a favorite inclusion in older manuals, does not seem a valuable addition to a restricted course. The final experiment, the preparation of indigo from benzaldehyde, requires an expansive reaction scheme to represent the unusual ring-closure involved, and is so special a preparation as to have little value except perhaps for advanced students.

The second part of the manual, devoted to the presentation of an abbreviated scheme of qualitative organic analysis, is introduced by preliminary remarks on small-scale laboratory operations. There is here some repetition of material in Chapter II (Important Laboratory Operations), and some further repetition of the same kind occurs in the introduction to the preparation of derivatives. It would seem more consistent to mass all special information as to operations on an analytical scale at the start of the qualitative section, or even to include it in Chapter II preceding the entire laboratory course. Methods for handling small quantities of material are frequently needed in preparative work.

The chapter on "Analytical Methods" includes quantitative procedures for determination of specific gravity, neutralization equivalent, and saponification equivalent. In the qualitative tests for elements two paragraphs are devoted to detection of possible cyanamide formed in the nitrogen test, though it is encountered "only relatively rarely." There follow a series of thirty numbered "Special Tests." These include tests of solubility, various familiar general or functional tests, and a number of tests for individual compounds. The inclusion of the Hopkins-Cole tryptophane test serves no very good purpose. The list of compounds appears to contain only one entry to which the test is applicable, *viz.*, "a protein," whose identification stops with the recognition of its probable protein character.

In the classified lists of compounds which follow there appear some three hundred compounds, for the most part common and inexpensive. The initial classification into orders is based on elementary composition. Further classification, into groups, is based on physical state at room temperature, and at one point solubility in water is used to effect a subdivision. Listed compounds are arranged within the appropriate order and group, in subdivisions based on a similar response to one or more of the general tests. Individual compounds in each division are arranged in the order of increasing melting or boiling points, and each name is accompanied by suggestions as to the numbered tests to be applied and the results to be expected. The list of compounds appears on the whole to be well chosen. Tyrosine and phenylalanine are rather expensive to be given out as unknowns in most schools, and carbon disulfide, phenyl isocyanate, and α-naphthyl isocyanate are not very good unknowns, especially as the last two are used as reagents.

The chapter on "Preparation of Derivatives" presents typical procedures for obtaining certain of the familiar types of derivatives. For each type a table of some individual derivatives and their melting points is given. These tables include derivatives of more than a few compounds not mentioned in the classified lists. The section on derivatives includes a relatively large number of special derivatives for single compounds, some of which could be identified readily by means of one of the general procedures. The presentation of these special derivatives is in some cases unduly expansive, due to explanations with formulas or reaction schemes. Salts of pseudobenzylthiourea are suggested as derivatives for carboxylic and sulfonic acids. These derivatives have melting points which are not well separated, and with improper handling may split out benzyl mercaptan by hydrolysis, both drawbacks, especially in a student course.

The analytical scheme employed in this manual is doubtless satisfactory for the conditions established, *i. e.*, when it is known that the substance is one of a list of several hundred compounds. It would be of little real help if the list were increased to several thousand compounds. Students unquestionably would derive benefit from experience with class reactions and the preparation of derivatives, as well as from the necessity for analytical thinking, however limited in scope the analytical "system" used, and for this reason the reviewer is inclined to the view that even a brief course is much better than none at all. If, however, approximately half of the laboratory time is to be devoted to qualitative organic analysis, it seems possible to use a more comprehensive qualitative system, of which several are available.

The value of the plan presented, *viz.*, the combination of abbreviated preparative and qualitative analytical courses into a single course, seems debatable. Any arrangement which includes qualitative analysis as part of the instruction in organic chemistry probably has merit, but whether or not it should be introduced by rather drastic reduction in the amount and scope of the preparative work may be left to the judgment of those who design organic courses.

The manual is with minor exceptions well and clearly written, and is almost free from misprints. Typography is excellent, though some structural formulas are unduly spread out. The future of this book, and of the idea it represents, may be awaited with interest.

E. C. WAGNER

UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA, PENNSYLVANIA

PORTRAITS OF EMINENT MATHEMATICIANS. *David Eugene Smith*, Professor Emeritus of Mathematics, Columbia University. *Scripta Mathematica*, 562 West 144th Street, New York City, 1936. 65 pp. 12 portraits. 36.5 × 27.5 cm. $3.00.

The portraits included in this portfolio are those of Archimedes (287–212 B.C.), Nicholas Copernicus (1473–1543), François Viète (1540–1603), Galileo Galilei (1564–1642), John Napier (1550–1617), René Descartes (1596–1650), Sir Isaac Newton (1642–1727), Gottfried Wilhelm Leibniz (1646–1716), Joseph Louis, Comte Lagrange (1736–1813), Carl Friedrich Gauss (1777–1855), Nicolai Ivanovitch Lobachevsky (1793–1856), and James Joseph Sylvester (1814–1897). The selection for publication was made from a large collection assembled over a long period for the Library of Columbia University by Dr. Smith, "with a view to strength, dress, character and achievements. In general, facsimiles of the handwriting of the mathematicians whose portraits appear are from the same collection."

The portfolio, which is a fine piece of work, will be of general interest because of the information contained in the biographies and the beauty of the format. One hopes that other collections of a like kind may follow the first one.

VIRGINIA GORE

EDITORIAL STAFF

PRINCIPLES OF BIOCHEMISTRY. *Albert P. Mathews*, Andrew Carnegie Professor of Biochemistry, University of Cincinnati. William Wood and Co., Baltimore, 1936. x + 512 pp. 15 × 23 cm. $4.50.

The purpose of this text is, as stated by the author, to present to medical students a coördinated picture of the principal facts and theories of biochemistry in a manner which will correlate and synthesize these facts and theories into a subdivision of a "great science which reveals the finer structure and coördinated chemistry of the human body." It has been the author's desire, also, to stimulate the imagination of the student to a realistic

conception of the subject. Both of these objectives have been admirably fulfilled. Dr. Mathews' profound knowledge of the subject, coupled with his well-known delightful and lucid style, has made him singularly fitted to write such a text. He does not hesitate to employ poetic conceptions of chemical processes in life. For example, in summarizing the formation and importance of phosphoric esters of glucose in body cells, he says, in part: "Phosphoric acid meets it (glucose) at the door; extends to it a hand; it is married to it by phosphatase (co-zymas), that universal clergyman; and escorts it through the cell. Glucose is now embarked, in the company of this phosphoric acid, on that exciting series of adventures, breath taking, which it undergoes in living matter, and which leads finally to its undoing and ultimate resolution into the elements of carbonic acid and water from which it arose." Of course, the text is not entirely in this vein, but similar passages occur not infrequently.

The text is divided into six parts as follows: Part 1, Chemistry and Metabolism of the Glucides. Part 2, Chemistry and Metabolism of the Lipides. Part 3, Chemistry and Metabolism of the Proteins. Part 4, The Special Chemistry of Important Tissues. Blood and Connective Tissues. Part 5, The Catalytic Agents of Growth and Development. Vitamins and Hormones. Part 6, The Income of Energy. Part 1 comprises the largest section of the text with fifteen chapters. Part 3 is second with eight chapters. The mineral metabolism of the body is the topic of the last chapter under the proteins. The reason for this arrangement is not given. Parts 2 and 4 have equal lengths of about seventy-five pages and six and eight chapters, respectively. About fifty pages are devoted to the vitamins and hormones in Part 5, while the subject of energy metabolism in Part 6 is treated very briefly in a single chapter of six pages. The enzymes are not covered in a separate chapter or section as is usually the case in biochemistry texts. Instead the enzymes are treated in connection with their several functions as related to metabolism of carbohydrates, lipides, and proteins, respectively.

The vitamins and hormones are especially well presented. In connection with the vitamins Dr. Mathews develops a very interesting and novel hypothesis that all the vitamins act in the body as enzymes, possibly in a manner identical with Warburg's "yellow enzyme," namely by first conjugating with protein through phosphoric acid. There is a very lucid presentation of the as yet unknown biochemical aspects of heredity in the chapter on hormones, the author emphasizing that the chromosomes comprise only one, possibly a minor aspect of the entire phenomenon of heredity. The probable importance of the hormones in heredity is well presented, especially the relation of the sex hormones to the determination of sex.

The text is not entirely free from errors in statements and conceptions, but none is of major importance. The reviewer also encountered a few contradictory statements. All of these will no doubt be corrected in a later edition.

This text is an outstanding contribution to the field of chemical education. It should be in the library of every biochemist and every teacher of biochemistry, as well as on the physician's book shelf, both student and practitioner.

LEROY S. PALMER

DIVISION OF BIOCHEMISTRY
UNIVERSITY OF MINNESOTA
ST. PAUL, MINNESOTA

THE THEORY OF THE PROPERTIES OF METALS AND ALLOYS. *N. F. Mott*, Professor of Theoretical Physics in the University of Bristol, and *H. Jones*, Lecturer in Theoretical Physics in the University of Bristol. Oxford University Press, London and New York. xiii + 326 pp. 108 figs. 15 cm. × 24.5 cm. $8.00.

This publication, the newest member of "The International Series of Monographs on Physics," has for its aim an account of the crystal structure, magnetic susceptibility, and electrical and optical properties of individual metals and alloys. There are seven chapters entitled:

I. Thermal Properties of the Crystal Lattice
II. Electrons in Equilibrium in the Crystal Lattice
III. Motion of Electrons in an Applied Field
IV. Cohesion
V. The Crystal Structure of Metals and Alloys
VI. Heat Capacity and Magnetic Properties of the Metallic Electrons
VII. The Electrical Resistance of Metals and Alloys

The book assumes a thorough mathematical approach to the subject matter, making use of quantum mechanics and atomic physics. According to the authors, "In this book we make no mention of that property of metals which is of the greatest technical importance, namely that of strength. It has not been possible to apply the methods of atomic physics to this problem. The properties of metallic surfaces are not discussed."

As far as the reviewer can ascertain the book is complete and accurate in its approach and conclusions. Those who are reluctant to apply the quantum theory to a study of the metallic state need only study the lucid triumphs of this theory in explaining the distinction between metallic conductors and insulators, in studies of the equation of state, cohesion, crystal structure, and magnetism to be convinced of its value and necessity. On pages 243 and 244, for example, the authors prove the dependence of resistance on temperature. "As we have seen in Chapter III, in a perfectly periodic lattice a beam of electrons moving in a given direction will continue to move in that direction indefinitely. *A perfect lattice has, therefore, no resistance whatever.* If, however, the lattice is not perfectly periodic, the electrons will eventually be scattered. It is from this scattering that resistance arises. To calculate the resistance, therefore, our problem, just as in the classical theory, is to obtain the probability of scattering and hence the time between collisions 2τ and the mean free path l ..... We shall take an Einstein model for the metal crystal, supposing each atom to be able to vibrate about its mean position with frequency ν; then the Einstein characteristic temperature is defined by:

$$h\nu = k\Theta \tag{4}$$

We denote the restoring force when an atom is displaced a distance $\mathbf{X}$ from its mean position by $-b\mathbf{X}$, so that the equation of motion of an atom is:

$$M\ddot{\mathbf{X}} + b\mathbf{X} = 0$$

where M is the mass of the atom. Therefore

$$b/M = 4\pi^2\nu^2$$

If $\overline{\mathbf{X}}^2$ denotes the mean square of the displacement in a given direction, we have

$$^1/_2 b\overline{\mathbf{X}}^2 = \text{mean potential energy} = {}^1/_2 kT \tag{6}$$

for temperatures above the characteristic temperature; for lower temperatures

$$^1/_2 b\overline{\mathbf{X}}^2 = \frac{^1/_2 h\nu}{e^{h\nu/kT} - 1} \tag{7}$$

"Now, as we have stated above, an electron may be scattered by a displaced atom, and it will be shown below that the probability for scattering is proportional to $\mathbf{X}^2$, *i. e.*, to the square of the displacement. Since the resistance R of a metal is proportional to the scattering probability, we may write:

$$R \propto \overline{\mathbf{X}}^2 \tag{8}$$

But from (4), (5), and (6) for $T \gg \Theta$

$$\overline{\mathbf{X}}^2 = kT/b = h^2T/4\pi^2Mk\Theta^2$$

whence, from (8)

$$R \propto T/M\Theta^2 \tag{9}$$

We thus obtain the result that at high temperatures the resistance is proportional to the absolute temperature."

This contribution to the literature of the physics of metals must be considered too advanced for the average undergraduate in chemistry, physics, or metallurgy. The advanced student in atomic physics and the X-ray metallographer will find it a necessary adjunct to his thorough understanding of the theory of

metals and alloys. It should be considered as an essential addition to any serious library on the subject. Modern and up-to-date in material, it is cognizant of all the important work and theories of foreign and English investigations in this direction. The fact that there are so many references to articles published this year is proof of its thoroughness.

The book is beautifully bound and printed. The figures and illustrations are good and carefully chosen to assist the mathematical and theoretical derivations and explanations. A number of tables give valuable information.

FREDERICK A. ROHRMAN

MICHIGAN COLLEGE OF MINING AND TECHNOLOGY
HOUGHTON, MICHIGAN

A LABORATORY MANUAL OF GENERAL CHEMISTRY. *Herman T. Briscoe*, Professor of Chemistry, Indiana University; *Herschel Hunt*, Assistant Professor of Chemistry, Purdue University; and *Francis M. Whitacre*, Assistant Professor of Chemistry, Case School of Applied Science. Houghton Mifflin and Co., Boston, 1936. 274 pp. 23 figs. 6 tables. 22 × 28 cm. $1.75.

Three covers of water-resistant cardboard, a study guide, and a notebook are all made into a single book by an ingenious application of spiral binding. When laid flat three pages may be seen at one time, so that the student may read directions for experiments, questions and the like, and at the same time see the forms provided for the entry of results. The manual is intended for use in classes where the students have had or have not had high-school chemistry. Optional experiments are provided for the abler students. The book provides work for one full year of at least four laboratory periods a week.

The first half of the book is made up of a study guide of directions for fifty-three units of experimental work and an appendix of eleven pages. The units are alike in their general makeup. Each consists of an introductory explanation, directions for the conduct of experimental work and review questions intended to direct the students' attention to important facts or to introduce new problems, the solution of which will lead to a better understanding of the principles involved. Most of the experimental work is quantitative in nature, and the questions tend to emphasize the quantitative aspects of chemistry. The appendix of eleven parts designated by letters is intended to aid the student in the solution of mathematical problems and to supply data which he could not be expected to know. Appendix A consists of explanations of sixteen types of problems, with the solution of one example of each. Appendixes B, C, D, E, F, and G are useful tables. Appendix H is an apparatus list representing a larger kit of apparatus than is usually supplied to the college freshman. Appendix I is a list of all chemicals needed for each experiment (something very helpful to the laboratory instructor). Appendix J is a table of references to twelve of the more recent college textbooks in general chemistry, and Appendix K describes laboratory precautions in detail and gives directions for first aid in case of accident.

The second half of the manual is in reality a notebook with removable pages and definite places for the entry of all data, calculations, and experimental work. Each page is marked and numbered to indicate the experiment to which it relates. This arrangement is a valuable aid to the instructor when he grades or corrects the notebooks. Carefully worded questions are intended to lead the student to reflect on the meaning of phenomena observed and to connect these with the principles and laws to which they are related. This work has been well done indeed.

In general, it can be truthfully said that this book represents an advance over most manuals now available for use in first-year classes. Special thought has been given to the teaching of those items which are most frequently poorly taught, and less attention is given to materials usually well presented by demonstration in the class room. Yet there is no serious reduction in "first hand contacts" with the actual materials, apparatus, and processes of general chemistry which are essential to intelligent textbook study.

The arrangement and presentation of each unit is such as to justify the authors' contention that it provides more time for observation, reflection, and interpretation of results, makes the recording of data more uniform and easily read, and saves the instructor time and labor in grading.

This manual should be given careful consideration by all college teachers of general chemistry.

J. O. FRANK

STATE TEACHERS COLLEGE
OSHKOSH, WISCONSIN

A COMBINED LABORATORY MANUAL AND WORKBOOK IN CHEMISTRY. *Kenneth E. Conn*, Head of Chemistry Department, High School, Bloomington, Indiana, and *Herman T. Briscoe*, Professor of Chemistry, Indiana University. Mentzer, Bush and Company, New York City, 1935. xvi + 429 pp., including numerous blanks, detachable, punched. 53 figs. 18.5 × 25.5 cm. $0.80, less discount.

The combined laboratory manual and workbook is written on a basis of twenty-five subject-matter units. Each unit contains: (1) preliminary questions, (2) preview, (3) experiment(s), (4) self-administering tests, (5) study outline, (6) bibliography. The pupil who studies a unit from these five different approaches should become thoroughly conversant with the contents.

The preliminary questions are to be used both before and after the study of the unit and are in general designed to be thought-stimulating. The preview contains a relevant quotation and a brief, interesting introduction to the unit. The experiments are simple, require simple apparatus, and are to be recorded by answering direct questions in short sentences. The self-administering tests and study outlines are frequently of the new type, although this is not always the case. Multiple choice tests are employed most often. The bibliography is limited to a relatively small number of reliable sources. References to fourteen widely used textbooks are included, so the combined workbook and manual can fit practically any teaching situation. The strongest appeal of this book is in the carefully worked out questions based on test-tube experiments chiefly. The student is not led to assume more than the evidence warrants, showing an excellent example of an application of one phase of the scientific method of thinking. Especially good are the experiments of a practical sort, those dealing with paints, electroplating, nitrocellulose, digestion, and dyeing. Each experiment is printed in such a way that it may be removed from the book without destroying a portion of another exercise.

Additional exercises and experiments are provided for the benefit of ambitious pupils, and a brief course in the qualitative analysis of the cations is included near the end of the book. The book is quite free from serious errors and is good mechanically. One wishes, however, that the subscript numbers in formulas were in much larger type.

The range of phenomena studied under a given unit is not as extensive as that in several workbooks now available. Therefore, the chance of a pupil's finding the workbook questions answered in a given textbook is good.

CHEMISTRY TESTS, FORM A. *Kenneth E. Conn*, Head of Chemistry Department, High School, Bloomington, Indiana, and *Herman T. Briscoe*, Professor of Chemistry, Indiana University. Mentzer, Bush and Company, New York City, 1933. 59 pp. 18.5 × 25.5 cm. $0.20, less discount.

This pamphlet is a set of tests, chiefly new-type, including mid-year and final examinations, to accompany the *"Combined Laboratory Manual and Workbook"* by the same authors. No information is furnished as to the standardization or reliability of these tests.

ELBERT C. WEAVER

BULKELEY HIGH SCHOOL
HARTFORD, CONNECTICUT

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128 Illus. 631 Pages. Cloth $10.00

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TRADE ANNOUNCEMENTS

Lawrence College Expands Chemical Laboratories

Lawrence College is undertaking a complete rehabilitation of its chemical laboratories with the purpose of providing modern laboratories on a par with those of any educational institution in the Central West, according to an announcement made by the *Kewaunee Manufacturing Company, Kewaunee, Wisconsin*, who have been retained to provide new laboratory furniture and equipment throughout the Department.

The laboratory furniture and equipment throughout will embody the latest technological advances in the laboratory furniture industry, and has been designed with a view of securing for Lawrence College one of the best equipped groups of chemical laboratories available in the educational field.

A qualitative and general organic laboratory, a quantitative and physical chemistry laboratory, and an organic chemistry laboratory are included, as well as completely modern stock departments, private laboratories, dark room, preparation rooms, balance rooms, reception lobby, and a very attractive and well-equipped lecture room.

The national interest which has been aroused by the accomplishments of the Institute of Paper Chemistry, affiliated with Lawrence College, and the outstanding graduate and research work of the Institute have tended to make Lawrence a center for chemical education, and the new laboratories in the Stevenson Hall of Science, it is expected, will greatly further activity in this department of the College.

Radio Sets Now Used on New York Central Trains

Radio-minded passengers on the Twentieth Century and Southwestern Limiteds and other crack New York Central trains are now able to listen in on important broadcasts, such as election returns and major sports events, while skimming across country at high speeds, as the result of an unusual receiver-installation system recently established for these trains, it was announced recently by L. W. Landman, general passenger traffic manager of the railroad.

To provide rail travelers with this modern feature, a battery of twenty of the larger home-type console sets manufactured by the *General Electric Company* and operated much like those that passengers are accustomed to use in their own residences, is kept instantly available at a central point so that when an important event is to be broadcast the sensitive receivers, each employing twelve of the new metal tubes, can be readily distributed among the major trains in service that day. In addition, the procedure followed in making the installations has been systematized in such a way that the complete radio equipment, including antenna, can be put in place and made ready for operation on very short notice.

Usually, at the end of the run, the equipment is removed to await the broadcast of another important event, but it may be left installed if circumstances so dictate. It was planned to provide this radio service on both November 3 and 4 so that passengers might hear the results of the election.

Using a home-type receiver on a train involves several problems. First, the train power supply must be converted from 32-volt direct current to 110-volt alternating current, and this is accomplished by means of a small motor-generator set. Second, considerable radio interference is set up by various electric equipment operated on the train and along the right-of-way, and it is therefore necessary to employ a specially shielded antenna and lead-in system and filter condensers to "damp out" these disturbances. The antenna consists of a loop on the roof of the car of heavily insulated wire capable of withstanding a 15,000-volt "breakdown" test. The shielded lead-in cable runs from the ends of the loop to the receiver. This system of installation affords a quality of reception comparable to that obtainable in the home.

New Explosion-Proof Gearmotors

A new line of single reduction explosion-proof gearmotors ranging in size from $1^1/_2$ to 75 horsepower have been announced recently by the *Westinghouse Electric and Manufacturing Company*. Where speed reduction is required these gearmotors have many uses because of their compact design and high efficiency. Built to carry the maximum torque the motors will develop, the gears are of the single helical type, heat treated by a special "tough hard" process to provide maximum load-carrying capacity and utmost resistance to wear and shock. Anti-friction bearings assure high efficiency and maintain correct gear center distances.

They are inspected and approved by the National Board of Fire Underwriters for use in hazardous atmospheres containing gasoline vapors and other gases or vapors having equivalent or less hazard. Also, they are for use in dry-cleaning and dry-dyeing plants, pyroxylin plastic manufacturing plants, spray painting establishments, gas plants, varnish manufacturing plants, and other applications involving similar hazardous processes.

Trade Periodicals

CENCO NEWS CHATS, No. 11. *Central Scientific Co., 1700 Irving Park Blvd., Northcenter Station, Chicago.* 15 pp., 19.5 × 27.5 cm.

TRENT LEAFLET TC-30 of *Harold E. Trent Co., 618–640 North 54th St., Philadelphia.* Pp. 9–10, 20 × 28 cm.

DUTCH BOY PAINTER MAGAZINE. Vol. 29, No. 4, 1936. *National Lead Company, 111 Broadway, New York City.* Pp. 75–94, 14 × 19.5 cm. Copies will be mailed without charge to painters and paint dealers.

NICKELSWORTH, Vol. 1, No 2, 1936. *International Nickel Company, Inc., 67 Wall St., New York City.* 8 pp., 21.5 × 28 cm.

THE NEW JERSEY ZINC ALLOY POT, Vol. 4, No. 4. *The New Jersey Zinc Company, 160 Front St., New York City.* 8 pp., 21.5 × 28 cm.

BRIMSTONE BREVITIES, No. 3, November, 1936. Issued from time to time by the *Freeport Sulphur Company, 122 East 42nd St., New York City.* Pp. 25–36, 21.5 × 28 cm. The publication contains original articles, quotations, and literature references bearing on the many uses of materials in which an important constituent is sulfur, with particular emphasis on its place in agriculture.

Trade Literature

SUPPLEMENT TO A VISUAL REPORT OF PROGRESS. *The New Jersey Zinc Company, 160 Front St., New York City.* 32 pp., 22 × 28 cm. Profusely illustrated.

Copies of A VISUAL REPORT OF PROGRESS are still available. A technical discussion of the Zinc Alloys of the Zamak type which have been developed in the Research Laboratories of *The New Jersey Zinc Company* is included in the Research Bulletin, Zamak Alloys for Zinc Alloy Die Castings.

MONEL AND NICKEL IN GAS WORKS, BULLETIN C-5 of *The International Nickel Company, Inc., 67 Wall St., New York City.* 20 pp., 21.5 × 28 cm.

OPTICAL INSTRUMENTS, Catalog L-2 of *The Gaertner Scientific Corporation, 1201 Wrightwood Ave., Chicago.* 80 pp., 19 × 26.5 cm.

INDUSTRIAL USES OF MICARTA. *Westinghouse Electric & Manufacturing Company, Micarta Works, Trafford, Pennsylvania.* 24 pp., 21 × 28 cm.

THE IMPROVED KW WIDE FIELD BINOCULAR MICROSCOPE. *Bausch & Lomb Optical Co., Rochester, New York.* 4-page folder. 15.5 × 23 cm. Illustrated.

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